DEC 10 1935

DO NOT TAKE FROM LIBRARY

copy 2

THE PHYSICAL REVIEW

VOLUME 48 *Second Series* NUMBER 11

DECEMBER 1, 1935

Published for the

AMERICAN PHYSICAL SOCIETY

by the

AMERICAN INSTITUTE OF PHYSICS
Incorporated

LANCASTER, PA., AND NEW YORK, N. Y.

THE AMERICAN PHYSICAL SOCIETY

OFFICERS OF THE SOCIETY

R. W. WOOD, *President*
The Johns Hopkins University
Baltimore, Maryland

F. K. RICHTMYER, *Vice President*
Cornell University
Ithaca, New York

W. L. SEVERINGHAUS, *Secretary*
Columbia University
New York, New York

G. B. PEGRAM, *Treasurer*
Columbia University
New York, New York

JOHN T. TATE, *Editor*
University of Minnesota
Minneapolis, Minnesota

L. B. LOEB, *Local Secretary for the Pacific Coast*
University of California
Berkeley, California

THE PHYSICAL REVIEW

BOARD OF EDITORS

JOHN T. TATE, *Editor*

J. W. BUCHTA, *Assistant Editor*

Associate Editors

K. K. DARROW
J. C. HUBBARD
A. E. RUARK
A. ELLETT
L. A. TURNER
G. E. UHLENBECK
W. V. HOUSTON
R. S. MULLIKEN
I. I. RABI

THE PHYSICAL REVIEW, which was established in 1893, is a journal of experimental and theoretical physics. It is published for the American Physical Society by the American Institute of Physics Incorporated. There are two volumes annually with twelve issues in each volume.

Manuscripts for publication should be submitted to John T. Tate, University of Minnesota, Minneapolis, Minnesota.

Proof and all correspondence concerning papers in the process of publication, should be addressed to the Editorial Secretary, American Institute of Physics, 11 East 38th Street, New York, New York.

Subscription price: United States and Possessions and Canada, $15.00; Foreign, $16.50. Subscriptions and orders for back numbers should be addressed to Prince and Lemon Streets, Lancaster, Pennsylvania, or to the American Institute of Physics, 11 East 38th Street, New York, New York.

Advertising is not accepted for the *Physical Review* but attention is called to the *Review of Scientific Instruments with Physics News and Views*, a companion publication of the Institute, and a medium through which the field of physics can be reached most effectively. Rates and other information will be furnished on request to the Editorial Secretary.

Changes of address and complaints of failure to receive the *Physical Review*, in the case of members of the American Physical Society, should be addressed to the Treasurer; in the case of other subscribers, to the Editorial Secretary. New copies can be sent free in response to complaints of non-delivery only if notice of non-delivery is received within three months of date of issue.

The Physical Review is published semi-monthly at Prince and Lemon Streets, Lancaster, Pennsylvania.

Entered at the Post Office at Lancaster, Pennsylvania, as second class matter.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorised September 6, 1926.

THE
PHYSICAL REVIEW
A Journal of Experimental and Theoretical Physics
VOL. 48, No. 11 DECEMBER 1, 1935 SECOND SERIES

Search for Radioactivity Induced by 800-Kilovolt Electrons

J. J. LIVINGOOD AND ARTHUR H. SNELL,* *Radiation Laboratory University of California*
(Received September 17, 1935.)

A filament is mounted on the high voltage end of a Sloan radiofrequency resonance transformer and electrons are accelerated out of the vacuum tank through a thin window at a maximum energy of about 850 kv. About fifty elements have been bombarded with these electrons and examined with a Geiger counter for induced radioactivity. No positive results were obtained. This indicates that the yield is less than 1 activation per 10^{12} electrons of approximately 750 kv, provided that the half-lives have values between some seconds and one or two hours and that the products of disintegration are electrons of over 200 kv energy. The collision cross sections for such reactions have upper limits ranging from 10^{-35} cm^2 for hydrogen to 10^{-33} cm^2 for uranium.

INTRODUCTION

IN the course of development of the Sloan radiofrequency high voltage resonance transformer for the purpose of generating x-rays and for the acceleration of positive ions, it seemed worth while to convert the apparatus into a Lenard tube, so that electrons could be directed outward into the room where they might be conveniently used. High voltage Lenard tubes have been studied in some detail by Coolidge[1] but, as far as we are aware, cathode rays have never been used in an endeavor to assail the nucleus. Theoretically one would expect them to have little or no effect, since the de Broglie wave-length of an electron traveling with approximately the velocity of light is still several powers of ten larger than the nucleus. Furthermore, since the Fermi theory of β-emission postulates the simultaneous emission of a neutrino, one would expect that the reverse process would require the double entry of an electron and a neutrino into the nucleus. If, on the other hand, it were found experimentally possible to make a nucleus become a β-emitter by first driving only an electron into it, the Fermi postulate would seem to require some modification.

APPARATUS

The principles of a radiofrequency high voltage generator have been described by its designer[2] and its performance as an x-ray tube has been published.[3] It is therefore necessary here only to recall that it consists of a powerful short wave oscillator feeding into a single resonant circuit which consists of a single loop primary and a large water-cooled secondary coil both suspended in an evacuated metal tank. The secondary coil acts as a quarter wave-length antenna; its voltage node is at its upper end where it is attached to the grounded tank, and its voltage

* 1851 Exhibition Scholar.

[1] Coolidge, Science **62**, 441 (1925); J. Frank. Inst. **202**, 693, 722 (1926). Gen. Elec. Rev. **35**, 413 (1932).

[2] D. H. Sloan, Phys. Rev. **43**, 213 (1933); **47**, 62 (1935).

[3] Stone, Livingston, Sloan and Chaffee, Radiology **24**, 153 (1935); **24**, 298 (1935).

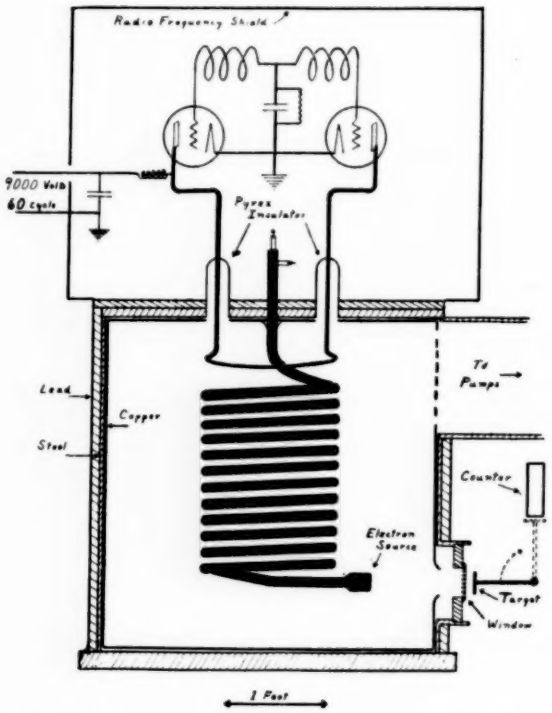

FIG. 1. High voltage radiofrequency resonance transformer, adapted for the acceleration of electrons.

loop is at the lower freely hanging end which executes high frequency oscillations, of about 44 meters wave-length, with an amplitude of some hundreds of kilovolts. When used as an x-ray tube, an anode is mounted on this high voltage end of the coil and a filament is placed at ground potential in the wall of the tank. Surrounding the filament is a grid several thousand volts negative with respect to it, so as to prevent the emission of electrons until the anode has neared the peak of its positive voltage oscillations, thus permitting an approximation to d.c. operation. To convert the apparatus into an electron accelerator of the Lenard type it was necessary to supply a source of electrons at the end of the high voltage coil and to mount a suitable window in the wall of the tank to allow the electrons to escape into the air of the room.

An early attempt at an electron source was simply an eighth-inch tungsten rod sharpened to a point and mounted on the end of the coil; as the voltage rises to a critical value cold emission sets in because of the intense electric field, and the source thus supplies its own bias to prevent emission at low voltage. This device, however, was unstable with regard to quantity and quality of emission, the sharpness of the point being quite critical, and the vacuum had to be lost for every adjustment.

Consequently advantage was taken of the construction of the main coil in order to mount a hot filament at its end. The coil is made of 7/8-inch outside diameter copper tubing within which is a copper tube of 7/16-inch diameter, the latter being covered with a layer of rubber tape to prevent heat transfer from the outgoing to the incoming water; the rubber is protected against erosion by a layer of thin copper tape. The two concentric pipes are therefore insulated from each other and serve admirably as lead wires to conduct current to the filament from a transformer at ground potential. The filament assembly is shown in Fig. 2; a copper glass seal and a tungsten glass seal are used to bring a connection from the inner tube out to the vacuum, the 0.080-inch tungsten rod being connected to the central pipe by a flexible wire for ease in assembly. The glass is protected from high frequency dielectric hysteresis and from cathode

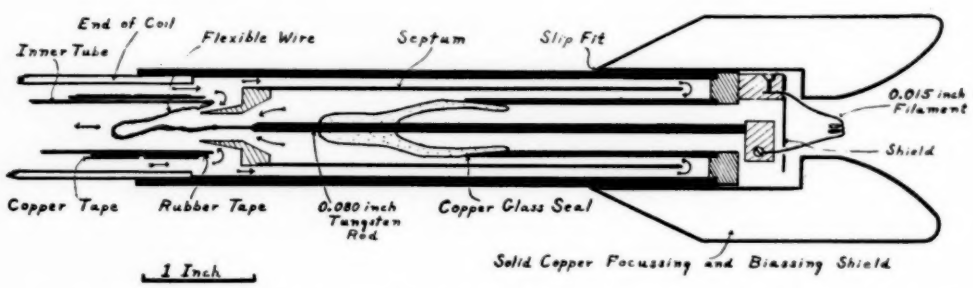

FIG. 2. Details of the filament assembly at the high voltage end of the transformer. The longitudinal hard rubber strips which align the septum have been omitted in the sketch for greater clarity. The direction of the water flow is indicated by arrows.

rays by the surrounding copper tube and by a small shield at the base of the filament. A thin cylindrical metal septum, held in place by longitudinal hard rubber strips (not shown in the figure), directs the water down to the end of the assembly, thus preventing stagnation and consequent boiling. By moving the rounded solid copper tip forward or backward the space charge around the filament can be considerably altered so that emission during the low parts of the voltage waves can be reduced. The filament is 20 cm from the tank wall.

This arrangement, though satisfactory, is not as good nor as flexible as would be an independently biased grid whose potential is controlled by a high voltage wire passing down the inside of the coil, but there are difficulties in obtaining a sufficiently well insulated wire that is small enough not seriously to hinder the flow of water. An alternative possibility would be to build into the filament unit a midget transformer, rectifier tube and filter condenser to supply the potential for a grid, driven through a circuit consisting of the main coil and a low voltage wire inside it.

The window for the electrons consists in a copper foil 0.001 inch thick soldered to a copper plate 2 inches in diameter and 3/16 inch thick and perforated by many 1/8-inch holes spaced 5/32 inch between centers. A water-cooling pipe is silver soldered to the periphery of this disk, which in turn is soldered to a larger brass plate attached with sealing wax to an aperture in the tank wall. The electron beam strikes the window over an area about 1 inch in diameter and currents of 300 microamperes (average, read on a d.c. meter) have been passed through without damage. Windows with larger holes covered with copper, nickel or molybdenum foils melted through in a few seconds, even though additionally cooled with jets of air or water. Scattering of the electrons in the foil and air is sufficient to bend the beam backwards so that a hemispherical glow can be seen, in the darkened room, of about six feet radius. All sealing-wax joints and rubber tubes in the immediate vicinity of the window must be shielded with metal, else a very rapid deterioration sets in due to the bombardment.

Knowledge of the energy of the electrons has been gained by rather rough absorption measurements. A plane collecting plate was mounted on an insulated stand about 2 inches from the window and connected to ground through a microammeter; absorbing foils of aluminum were placed between it and the window. To prevent the registration of electrons scattered around the foils, the collecting electrode was shielded with a diaphragm consisting of a large sheet of 1/4-inch lead with a 1-inch hole cut in it. Correlation between range and energy was made through the data of Varder,[4] the maximum range of 0.048-inch aluminum indicating an energy of 845 kv. To obtain this potential, the average power dissipated as heat in the coil, determined from the temperature rise of the cooling water, was 22.5 kw. The anode power supply (60-cycle a.c. at 9000 volts) totalled 70 kw, including the energy lost in the control resistances. The heating current for the oscillator filaments required 15 kw additional. Absorption curves were taken at a number of potentials applied to the anodes of the oscillator tubes and the heat dissipated in the coil was noted in each case. Comparison between the voltage developed (electron range plus window correction) and the power in the coil shows that these two quantities are quite well related by the equation

$$\text{Kilovolts}_{(\text{coil})} = 183\ (\text{Kilowatts}_{(\text{coil})})^{\frac{1}{4}}.$$

This form of equation was to be expected from elementary considerations, although the experimental value of the constant, of course, depends upon the inductance and capacity of the particular coil and vacuum tank used, as well as on the frequency and wave shape.

Search for Nuclear Disintegration

Because of the large intensity of the incidental x-rays, it was feasible at this time to search only for delayed radioactivity of targets bombarded by the electron beam after the exposure had been made and the high voltage shut off. The points of unprotected Geiger counters (connected to an amplifier and scale of two thyratron recorder) were quickly rendered unstable and useless by scattered electrons, even though no potential was applied to the point during bom-

[4] Varder, Phil. Mag. **29**, 726 (1915).

TABLE I. *Elements bombarded and examined for radioactivity.*

Z		Form Used	Z		Form Used
1	H^1	H_3PO_4	34	Se	Metal
1	D^2	D_3PO_4	35	Br	KBr
3	Li	Metal	38	Sr	$SrCl_2$
4	Be	Metal	40	Zr	Metal
5	B	Pyrex, borax	41	Cb	Metal
6	C	solid	42	Mo	Metal
7	N	$Ca(NO_3)_2$	47	Ag	Metal
8	O	Various compounds	48	Cd	Metal
9	F	$Ba F_2$	50	Sn	Metal
11	Na	NaCl	51	Sb	Metal
12	Mg	Metal	52	Te	Metal
13	Al	Metal	53	I	KI
14	Si	Glass, sand	56	Ba	BaF_2
15	P	H_3PO_4	58	Ce	$Ce(NO_3)_3$
16	S	Solid	60	Nd	$Nd(NO_3)_3$
17	Cl	NaCl, KCl	73	Ta	Metal
19	K	KCl, KI	74	W	Metal
20	Ca	CaO, $Ca(NO_3)_2$	78	Pt	Metal
24	Cr	$K_2Cr_4O_7$	79	Au	Metal
25	Mn	$MnCl_2$	80	Hg	Hg–Cu amalgam
26	Fe	Metal	81	Tl	Metal
27	Co	$CoCi_2$	82	Pb	Metal
28	Ni	Metal	83	Bi	Metal
29	Cu	Metal	90	Th	$Th(NO_3)_4$
30	Zn	Metal	92	U	$U(NO_3)_3$
33	As	As_2O_3			

bardment. Consequently, lead shielded counters were used and a system of levers and control strings arranged such that the operator could move the target into the electron beam and close the opening to the counter or, after the exposure, open the counter and swing the target into position in front of it. This shift could be made within two seconds, from the operator's station in a lead shielded booth across the room. Some of the targets were in the form of metallic disks, others as powder held to a base plate with a thin layer of sealing wax. All of the latter type and many of the former had to be water cooled. The targets were bombarded for three minutes and examined with the counter for five minutes, this procedure being repeated several times for each. The electrons of all velocities totalled about 100 microamperes and the usual peak energy was somewhat over 800 kv.

Table I lists the elements bombarded and examined. In no case was there any evidence of induced radioactivity.

At a very conservative estimate, based on the absorption curves, at least 1 microampere of the bombarding electrons had an energy of 800 kv or over. Counts numbering three times the background would certainly have been recognizable so that, taking into account the solid angle subtended by the counter, a yield of 1 disintegration per second would have been significant, provided that the half-lives were not shorter than about a second nor longer than perhaps an hour, for the bombardments of each element totalled about 10 minutes, and 2 seconds were lost before counting began. If it be assumed that the products of disintegration are electrons of not less than 200 kv energy, they could emerge from the target and reach the counter after starting from a depth as great as that corresponding to 0.043 gram/cm², in which thickness the 800 kv bombarding electrons are reduced in energy to 710 kv. We may conclude, therefore, that if electrons of approximately 750 kv produce radioactive nuclei of half-lives measured by a few minutes and emitting β-particles of 200 kv energy or over, the efficiency is not more than 1 disintegration for 10^{12} electrons and that the collision cross sections range in value from not greater than 10^{-35} cm² for hydrogen to 10^{-33} cm² for uranium.

Pokrowski[5] has stated that x-rays of 90 to 140 kv produce radiations from lead; the activity reported was irregular and although it decreased rapidly in the first few hours following exposure, it apparently accumulated in intensity over many days of intermittent activation. Therefore in the present work not only was lead examined in the routine manner of the other elements, but a piece of lead from the shielding around the vacuum tank was investigated, after it had been exposed to the x-rays produced during several weeks operation. No counts above background were observed even when the lead was placed so close to the counter that particles of 2-mm range would certainly have been detected.

It is a pleasure to acknowledge the friendship and enthusiastic support of Professor E. O. Lawrence. One of us (A.H.S.) is grateful to the Royal Commissioners of the Exhibition of 1851. The experiments have been aided by grants from the Research Corporation and the Chemical Foundation.

[5] Pokrowski, Phys. Rev. **38**, 925 (1931).

Two Radioactive Substances from Magnesium after Deuteron Bombardment*

M. C. HENDERSON, *Radiation Laboratory, Department of Physics, University of California*

(Received September 16, 1935)

Under bombardment by 3.3 MEV deuterons, magnesium becomes radioactive with the emission of negative electrons and gamma-rays, and with two decay periods: $10\frac{1}{4}\pm\frac{1}{4}$ min. and 15.8 ± 0.5 hours. These periods are characteristic of Mg^{27} (Fermi) and Na^{24} (Lawrence). The reactions producing these bodies are:

$_{12}Mg^{26}+_1H^2=_{12}Mg^{27}+_1H^1$; $\quad _{12}Mg^{27}=_{13}Al^{27}+\beta+\gamma$.

$_{12}Mg^{26}+_1H^2=_{11}Na^{24}+_2He^4$; $\quad _{11}Na^{24}=_{12}Mg^{24}+\beta+\gamma$.

The protons have not been looked for. The alpha-particles have a range of about 7 cm. The Mg^{27} beta-rays have 2.0 MEV maximum energy, and the accompanying hard gamma-ray has about 1.3 MEV energy. The voltage excitation functions of these two activities have been measured, and have been found to follow different laws. The Mg^{27} following the Oppenheimer and Phillips function and the Na^{24} the older Gamow function. At 3 MEV one atom becomes Na^{24} for each 9.6 atoms going to Mg^{27}. The thick target yield of Mg^{27} atoms is about 5 per 10^7 deuterons. The nuclear cross section (Mg^{26}) at 3 MEV is about 2.4×10^{-26}.

1. INTRODUCTION

IMMEDIATELY after the discovery by I. Curie and F. Joliot[1] that artificial radioactivity could be produced by alpha-particle bombardment, several laboratories followed up their suggestion that it might be produced by deuteron and proton bombardment as well. The first communication from this laboratory on this subject reported[2] the results of preliminary work with elements in the first two rows of the periodic table. It was found at that time that several of them showed strong radioactive properties after bombardment with 3-MEV deuterons. The ionizing radiations emitted were "particles of electronic mass," but were not identified as to sign. For magnesium the half-life obtained was about nine minutes.

Since these first observations the apparatus has been modified[3] so that it is now possible to bombard the target with the desired ion, either in vacuum or in air, and to remove it immediately for measurement without disturbing the vacuum in the ion production chamber. Last spring work with magnesium was resumed, with the object of measuring the half-life more accurately and investigating the activity more in detail.

2. APPARATUS

The source of deuterons was the large cyclotron in the Radiation Laboratory. At the time the magnesium work was carried on, it was adjusted to furnish deuterons of energy of about 3.3 MEV. The energy of the ions produced by a cyclotron can be approximately calculated from the magnetic field or from the wave-length employed, but for experimental purposes it is always measured by determining their range in air, after they have passed out of the apparatus through a thin aluminum window. During most of the runs this range was 11.5 cm, taken as corresponding to deuterons of about 3.36 MEV.

The target was in all cases a piece of magnesium ribbon of 99.97 percent purity. Before bombardment the surface was cleaned with emery paper and washed with petroleum ether to remove oil film. The first sample was bombarded in air, but all subsequent ones were bombarded in vacuum to avoid oxidation and contamination of the surface by radioactive oxygen.[4]

All the measurements of activity were carried out on the Lauritsen-type quartz fiber electroscope of simple design that has been used for nearly all the electroscope measurements in this laboratory. A thin aluminum window, against which the radioactive source was placed, admitted the beta and gamma-rays to the ionization chamber, and the absorption measurements

* Reported at the Los Angeles Meeting, June, 1935. Abstract 5.

[1] I. Curie and F. Joliot, Nature **133**, 201 (1934).

[2] M. C. Henderson, M. S. Livingston and E. O. Lawrence Phys. Rev. **45**, 428 (1934).

[3] E. O. Lawrence and M. S. Livingston, Phys. Rev. **45**, 608 (1934). See also diagram in Phys. Rev. **47**, 453 (1935).

[4] E. M. McMillan and M. S. Livingston, Phys. Rev. **47**, 452 (1935).

were carried out by placing aluminum or lead sheets between the source and window. Unfortunately the intensity of the radiations was not great enough to allow the source to be more than a few centimeters from the window, and consequently the geometry of the arrangement left something to be desired.

3. The Decay Periods

A thick target of magnesium was bombarded in air for about 10 minutes by an ion beam of 3 MEV energy and about 0.9 microampere intensity. At the end of the exposure the target was at once placed at the window of the electroscope. The measured activity, as a function of time, is plotted on a logarithmic scale in Fig. 1, upper curve. The half-life determined from the linear portion, after due allowance for the natural leak and background activity of longer life, is 10.25 ± 0.25 min. The points taken in the first eight minutes show a more rapid decay as a result of the presence of radio-oxygen, which was deposited from the air around the target during the bombardment.

After about an hour and a half the successive readings showed definitely the presence of some substance with a longer life: in fact the activity two hours after exposure was still 20 times the natural leak. The target was therefore replaced in the cyclotron and the bombardment resumed with a view to intensifying the long-lived activity. After waiting two hours for the ten-minute substance to decay completely, a reading of the residual activity was taken and the decay was then followed for the next 24 hours. The half-life proved to be 15.8 ± 0.5 hours. These two periods were checked several times in the course of later runs that were made for other purposes. The errors are conservatively estimated.

To determine the sign of the ionizing particles they were observed visually in a Wilson cloud chamber that was placed in a magnetic field of a few hundred gauss.[5] All the particles, both those from the ten-minute and those from the sixteen-hour activity, proved to be negative electrons. No positrons could be detected. This fact rules out a carbon contamination as a possible source

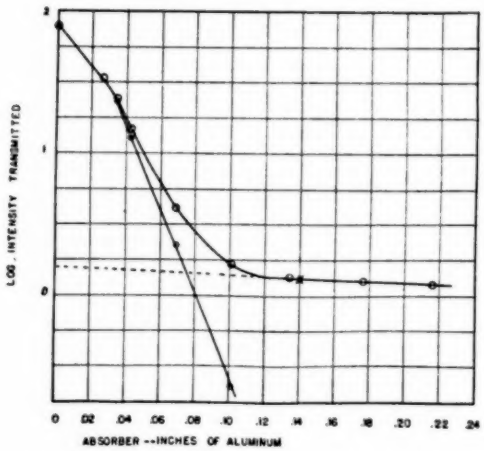

FIG. 1. Upper curve: decay of the activity of a magnesium target after deuteron bombardment. Lower curve: absorption of the beta-rays from Mg^{27} in Al.

of the ten-minute activity, since after deuteron bombardment carbon becomes radioactive with the emission of positrons.

4. The Active Substances

It is thus apparent that magnesium combines with deuterons to produce at least two radioactive substances. Their identity is at once apparent from the work of others, since the periods are characteristic of two substances already discovered: radio-sodium, Na^{24}, described by Lawrence,[6] having a half-life of 15.5 hours and produced by the action of deuterons on sodium; and radio-magnesium, Mg^{27}, discovered by Fermi,[7] half-life ten minutes and produced—among other ways—by the action of slow neutrons on magnesium.

Known types of reaction, when applied to the Mg^{26} isotope, lead at once to Mg^{27} and Na^{24}. Accordingly, we have:

$$_{12}Mg^{26} + {}_{1}H^{2} = {}_{12}Mg^{27} + {}_{1}H^{1};$$

$$_{12}Mg^{27} = {}_{13}Al^{27} + \beta + \gamma;$$

$$_{12}Mg^{26} + {}_{1}H^{2} = {}_{11}Na^{24} + {}_{2}He^{4};$$

$$_{11}Na^{24} = {}_{12}Mg^{24} + \beta + \gamma.$$

[5] I am indebted to Dr. Kurie for the use of the cloud chamber.

[6] E. O. Lawrence, Phys. Rev. **47**, 17 (1935).

[7] Fermi, Amaldi and others, Proc. Roy. Soc. **A146**, 483 (1934); Proc. Roy. Soc. **A149**, 522 (1935).

Many cases are now known in which the reaction between two nuclei leads to several pairs of end products. The two reactions just given are, however, the first in which two radioactive substances have been produced from a single substance by the use of a charged particle as a projectile. It seems reasonable to believe that this type of branching should be quite general and that not only Mg^{26} but also O^{18}, Ne^{22}, Si^{30} and other atoms may also yield more than one radioactivity under deuteron bombardment.

The protons emitted in the first reaction have not been looked for as yet. The alpha-particles, on the other hand, have already been observed, although their number was too small for accurate measurement.[8]

5. The Radioactive Radiations

The beta and gamma-rays from Na^{24} have been studied in detail by Lawrence (reference 6 and also unpublished work in this laboratory) and there seemed to be no point in repeating his experiments with an intrinsically weaker source. On the other hand, the beta-rays from Mg^{27} were measured by Fermi using a source obtained by neutron bombardment, and therefore necessarily much weaker than one obtained by the direct deuteron-magnesium reaction in the cyclotron.

An absorption curve of the radiation from a Mg^{27} source is shown in Fig. 1, lower curve. All points are corrected for decay and for natural leak. It will be seen that there is a component of hard radiation present along with the easily absorbed beta-rays. When this component is subtracted from the measured total intensity the steep linear curve results. Extrapolating this linear curve to the level of the natural leak gives for an "end point"—the maximum beta-ray range—the point marked with a cross. This end point falls at 0.95 g/cm² of Al. Using Feather's empirical rule—$E=(R+0.091)/0.511$, where E is in MEV and R in g/cm²—the maximum beta-ray energy is 2.05 MEV. Fermi found a half-value absorption thickness of 0.07 g/cm² in Al, in fair agreement with the data in Fig. 2.

The point corresponding to 2.05 MEV and 10.25 minutes, when placed on Sargent's curves of beta-ray periods and energies, lies midway between two branches. If the maximum energy were 3.8 or 1.2 MEV it would lie on one or the other of them, but the latter values seem to lie well outside the limits of experimental error.

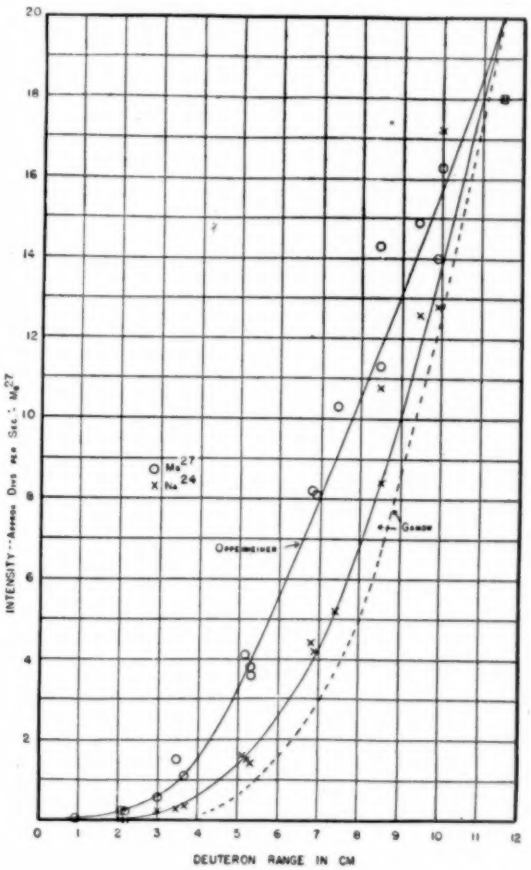

FIG. 2. The voltage transmutation functions of Mg^{27} and Na^{24}.

The absorption coefficient of the gamma-rays was determined in a separate experiment. A value of $\mu=0.74$ (cm^{-1}) of lead was obtained. The geometrical conditions were poor, but this value probably corresponds to an energy of about 1.3 MEV. From the intensity of the ionization produced by the gamma-rays, nearly 2 percent of that produced by the beta-rays, it appears that one gamma-ray is emitted for each beta-ray.

6. The Voltage Transmutation Function

The variation in the yield of transmutations as a function of the energy of the incident particle

[8] G. N. Lewis, M. S. Livingston and E. O. Lawrence, Phys. Rev. **44**, 55 (1933).

has been called the excitation function, or more properly the voltage transmutation function. The first theoretical treatment of this variation and a method for calculating it in any given case was first given by Gamow in *Atomic Nuclei and Radioactivity*. The formulas are obtained by considering, among other things, the variation with energy in the probability that the projectile as a whole penetrate the nucleus. For most of the reactions thus far studied, in which protons and alpha-particles are the projectiles, the formulas thus obtained fit the data well. However, it has been found in this laboratory[9] that the yield of transmutations caused by deuterons does not fit the Gamow curve at the higher values of deuteron energy, at least in the reactions in which a proton is emitted.

To meet this difficulty, Professor Oppenheimer and M. Phillips[10] have recently developed a theory for reactions of this type, one of the underlying assumptions of the theory being that the deuteron as a whole does not penetrate the target nucleus. Only the neutron in the deuteron enters the nucleus, the proton being "rejected." According to their calculations the transmutations should begin at a lower voltage than on the Gamow theory and should not increase as rapidly in number with increasing deuteron energy.[11]

Transmutations in which a radioactive body is produced are particularly convenient for studies of the transmutation function. Consequently, as soon as it was established that two radioactive bodies were obtained from magnesium, the attempt was made to measure the transmutation functions of both reactions. The measurement is particularly important because one of the bodies, Na^{24}, is produced by the penetration of the deuteron as a whole and the subsequent expulsion of an alpha-particle, while the other, Mg^{27}, is produced by the "rejection" of a proton and the absorption of a neutron. Thus the two activities should be different in their dependence upon voltage, the one following the older Gamow formula and the other the Oppenheimer theory.

Several runs were made to determine the transmutation functions by using the now standard method of exposing a pile of thin magnesium foils to the action of the deuteron beam and then separating the foils and measuring their activity separately. This method has several advantages: It gives the "differential" transmutation function directly, which is easier to compare with theory than the integral function; and it also ensures that all foils receive exactly the same exposure, since the deuteron beam passes through them all and since the number of deuterons that react in any given foil is a minute fraction of the total number passing through. The top foils in a pile thus act as absorbers to reduce the energy of the deuterons that reach the lower foils.

Magnesium is sufficiently malleable to be reduced with ease to foils a few ten-thousandths of an inch thick. The thickness was measured directly with a micrometer, and also more accurately, and for these experiments, more significantly by measuring their stopping power for polonium alpha-particles. For magnesium 0.001 inch is the equivalent of 2.5 cm of normal air (760 mm and 20°C). The thickness found convenient was about 1.4 cm of air, 0.00056 inch, or 0.0014 cm.

Before making an exposure each foil was carefully measured for thickness and was then stacked in a pile with a "mask" of thin copper sheet. This mask was placed on the pile to protect the edges of the foils from the deuterons and to prevent irregularities or cracks in the edges from allowing deuterons to leak through to lower members of the pile. After exposure in vacuum to about 0.8 microampere for $1\frac{1}{2}$ hours, the pile was removed, separated and the activity of each foil measured; the weakest first. After a lapse of two hours, sufficient to permit the Mg^{27} to decay completely, the foils were again measured for the Na^{24} activity. Since the Na^{24} activity was never more than about 1 percent of the Mg^{27} activity at the time the latter was measured, no correction has been applied for it. The activity of each foil, of each kind, was then corrected for decay since the end of the exposure and also corrected for any difference in thickness there might be between foils, since a thicker foil is proportionately more active.

[9] E. O. Lawrence, E. M. McMillan and R. L. Thornton—abstract in Science **81**, 421 (1935); Phys. Rev. **48**, 493 (1935).

[10] Oppenheimer and Phillips, Phys. Rev. **48**, 500 (1935).

[11] I am indebted to Professor Oppenheimer for calculating the yield curve according to his theory.

The results of the last three runs are shown in Fig. 2. To bring out the difference in transmutation function, all the activities have been made comparable by making the points at highest energy coincide. There are thus six experimental points at 11.5 cm and 18 div/sec. The ordinates for Na^{24} have been multiplied by approximately 200 to make this fit. The two solid curves are drawn in accordance with the two theories of the transmutation function, and have been adjusted to pass approximately through the mean of the points around 9 cm. The reason for using these points instead of the 11.5-cm point is that the top foil in a pile loses active atoms by recoil to the foil next beneath it, while the lower foils gain by this mechanism approximately as much as they lose.

It is readily seen that the transmutation function of the reaction producing Mg^{27} is quite different from the corresponding Na^{24} function, and the goodness of fit furnishes strong support to both theories.

The Gamow formula for the variation in number of transmutation, N, with voltage, V, is the following: $N=kV^{-1}e^{-S}$, where k is a constant of proportionality and S is defined by:

$$S=\left(\frac{4\pi e^2}{h}\right)\left\{Z_{Mg}\left(\frac{M_D}{2E_D}\right)^{\frac{1}{2}}+Z_\alpha Z_{Na}\left(\frac{M_\alpha\cdot M_{Na}}{2(M_\alpha+M_{Na})(Q+E_D^*)}\right)^{\frac{1}{2}}\right\}.$$

Z and M are the atomic numbers and masses, in grams, of the atoms indicated by the subscripts; Q, E_D and E_D^* are the energies, in ergs, of the transmutation, of the deuteron, and of the deuteron with respect to the center of mass of the system: i.e.,

$$E_D^*=E_D\cdot M_{Mg}/(M_D+M_{Mg}).$$

The first term inside the bracket takes account of the penetration of the deuteron through the nuclear barrier, the second term the penetration of the alpha-particle outwards through the sodium nuclear barrier. In actual numbers,

$$S=17.0/V^{\frac{1}{2}}+42.5/((14/13)Q+V)^{\frac{1}{2}},\quad V \text{ in MEV}.$$

In the calculation it is necessary to assume some value of Q, the energy of transmutation. An accurate knowledge of the range of the alpha-particles produced would of course lead at once to the value of Q. However, at the time the alpha-particles were found[8] the energy of the deuterons was only 1.2 MEV and the currents of the order of 10^{-8} ampere. A calculation from the Gamow formula and the yield found at higher energies shows at once that the number of alpha-particles to be expected under the old conditions was just on the limit of measurement, 2 or 3 a minute. Consequently no great accuracy is to be ascribed to the value found: 6 cm. A reconsideration of the data leads to 7 cm as the most probable value, corresponding to a Q of 8 MEV. More data are needed on this point.

In Fig. 2 two curves have been drawn for different Q's: the solid curve for $Q=10$ MEV, the dotted for 5 MEV. From the fit $Q=10\pm2$ MEV. Imperfections in the magnesium foils will lead to too high a value of Q.

One may also estimate Q from the masses and energies concerned. By writing the complete equations of the Na^{24} reaction and adding them:

$$_{12}Mg^{26}+{}_1H^2={}_{11}Na^{24}+{}_2He^4+Q.$$

$$_{11}Na^{24}={}_{12}Mg^{24}+\beta+\gamma.$$

$$(_{12}Mg^{26}-{}_{12}Mg^{24})+{}_1H^2-{}_2He^4=Q+\beta+\gamma.$$

The difference in mass between the two magnesium isotopes has not been accurately measured. In the parallel case of neon 20 and 22 the difference in mass is 1.998 ± 0.001.[12] One would offhand expect the Mg^{26} isotope to be about 2.000 heavier than Mg^{24}, since there are two more neutrons in the nucleus than are needed to form complete alpha-particles; but on the other hand, both the number of protons and the number of neutrons in both nuclei are even, so the general trend of the mass defect curve would lead to about 1.998 for the difference. Taking 2.000 ± 0.002 for this difference and Oliphant's values for H^2 and He^4, one gets $2.000+2.014-4.003=Q+\beta+\gamma\cdot=0.011\pm0.002$. From Lawrence's work[6] and from unpublished work in this laboratory, $\beta+\gamma$ is about 4 MEV, and hence Q is about 7 ± 2 MEV, in rough agreement with the value given by the Gamow curve.

In contrast with the Na^{24} reaction, no sensible

[12] Bainbridge, Phys. Rev. **43**, 424 (1933).

adjustment of the Gamow formula gives a fit with the Mg^{27} data. Even taking Q as infinite, tantamount to neglecting the second term in S, still gives a curve rising too steeply. The Gamow formula after making appropriate changes in the Z's and M's, becomes $S=17.0/V^{\frac{1}{2}}+12.3/((14/13)Q+V)^{\frac{1}{2}}$. The solid curve drawn through the Mg^{27} points has been calculated from the theory of Oppenheimer and Phillips[10] according to the equation (Eq. (12)). $N=kV^{-1}e^{-S'}$, where S' is defined as

$$S'=\frac{4Ze^2}{\hbar}\left(\frac{M}{I}\right)^{\frac{1}{2}}\overline{F(W/I)}.$$

In this equation, $\overline{F(W/I)}$ is the minimum value of $F(W/I)$, the values of which are taken from their plot of this function. I is the binding energy of the deuteron, $2M$ its mass, and W its kinetic energy. The only adjustable constant is the binding energy of the deuteron. This has been taken to be 2.0 MEV.

Although Q for the reaction in which Mg^{27} is produced does not enter the formula for the transmutation function, it is of interest to estimate it. As before, writing the equations of production and decay, one has:

$$_{12}Mg^{26}+{}_1H^2={}_{12}Mg^{27}+{}_1H^1+Q,$$

$$_{12}Mg^{27}={}_{13}Al^{27}+\beta+\gamma.$$

and adding them:

$$({}_{12}Mg^{26}-{}_{13}Al^{27})+{}_1H^2-{}_1H^1=Q+\beta+\gamma,$$

Al^{27} should be at least 1.000 heavier than Mg^{26} from the mass defect curve. Thus one has $-1.000+2.014-1.008=0.006$. $\beta+\gamma$ is about 3.3 MEV. Q is therefore about 3 MEV. This consideration supplies an upper limit to the mass of Al^{27}, since if $Q=0$, $Al^{27}-Mg^{26}=1.003$.

7. The Branching Ratios and the Absolute Yields

When a target is exposed to a constant beam of deuterons, any radioactive atoms that may be formed increase in number with the expression $(1-e^{-T/t_{av}})$. Consequently, after an exposure of two hours the number of Mg^{27} atoms in a magnesium target has practically reached a constant maximum value, while the number of Na^{24} atoms is only 8.5 percent of the maximum number. This maximum number represents, for each activity, a state of affairs in which as many atoms are being formed per second as are decaying. Since the number decaying per second is what is measured as "activity," the ratio of the final maximum activities is the ratio of the probability of formation of the two kinds of atom.

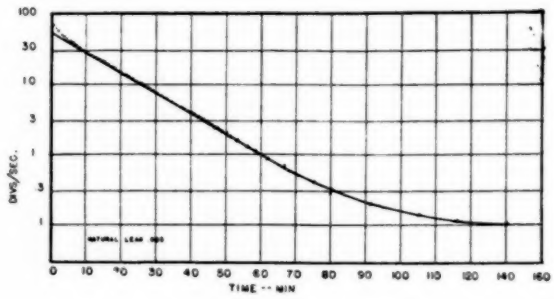

FIG. 3.

In one experiment the activities in the top foil, 1.4-cm air equivalent, at the end of a two hour exposure to 0.8 microampere were 19.5 div/sec. due to Mg^{27} and 0.18 due to Na^{24}. The saturation values of these activities, allowing for the finite time of exposure, are therefore 19.5 and 2.1. Hence for each atom of Na^{24}, $19.5/2.1=9.3$ atoms of Mg^{27} are produced. While this ratio is different at lower voltages, its variation with voltage may be readily calculated from Fig. 3.[13]

The absolute number of radioactive atoms produced is much more difficult to estimate accurately, depending as it does on the constancy of the deuteron beam, the transmission of the window, the calibration of the electroscope, and other factors. However, assuming a transmission of $\frac{1}{2}$—certainly too high—and the electroscope calibration of 2×10^4 beta-particles/sec. for 1 div/sec.; one finds that there are 1.6 Mg^{27} atoms produced for each 10^7 deuterons. The integrated yield, for a thick target, is about 3 times this, or 5 per 10^7.

Transmutation probabilities are often ex-

[13] In this and the other similar calculations no allowance has been made for the different energies of the Mg^{27} and Na^{24} beta-rays.

pressed in terms of the cross section of the nucleus, assuming that every deuteron which strikes within that cross section produces a transmutation and that all others do not. For Mg^{26}, 11 percent of the total number of atoms of Mg present, this cross section, from the data given, is 2.4×10^{-26} cm^2 at 3 MEV. Both this cross section and the yield as given above are certainly too low.

I am very greatly indebted to Professor Lawrence for the opportunity of using the cyclotron and for the facilities of the laboratory. To Professor Oppenheimer and Dr. McMillan I owe many thanks for helpful discussions and cooperation with some of the calculations. Thanks for financial assistance to the laboratory are also due the Research Corporation and the Chemical Foundation.

DECEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

The Infrared Absorption Spectrum of Germane

WENDELL B. STEWARD AND HARALD H. NIELSEN, *Mendenhall Laboratory of Physics, Ohio State University*

(Received September 30, 1935)

The infrared spectrum of GeH_4 has been measured to determine the fundamental vibration frequencies and to investigate the rotational structure of the bands. Intense absorption regions were found, enumerated in the order of their intensities, at 4.74μ (2110 cm^{-1}), 10.7μ (934 cm^{-1}), 3.4μ (2922.7 cm^{-1} and 3031 cm^{-1}) and 2.3μ (4300 cm^{-1}) which have respectively been identified as ν_3, ν_4, $\nu_1+\nu_4$, $\nu_3+\nu_4$, and $2\nu_3$. A much weaker absorption peak near 5.7μ is identified as $\nu_2+\nu_4$. From the spacings between the principal rotation lines in the fundamentals ν_3 and ν_4 a value 7.0×10^{-40} g-cm^2 for the moment of inertia of the molecule and values 1.37×10^{-8} and 2.06×10^{-8} cm, respectively, for the Ge-H and the H-H distances are indicated.

THE recent measurements on the infrared spectrum of methane[1] and silane[2] have shown that the observed bands conform very well in a general way with the predictions of the theory for molecules of the regular tetrahedral type, but that there exists a definite complexity of the rotational structure in many of the bands which is not readily accounted for. This lack of agreement between observation and theory and the obvious desirability of finding the values of the fundamental vibrations has seemed sufficient to warrant investigating the infrared spectrum also of germane (GeH_4) a molecule which also must certainly belong to the tetrahedral XY_4 type.

A sample of chemically pure GeH_4 was obtained as a gift from Professor Warren C. Johnston of the Department of Chemistry, University of Chicago. Like silane (SiH_4) this gas should be manipulated in the absence of air or oxygen to guard against explosions. Two absorption cells of glass fitted with windows of polished rocksalt were used, one 30 cm long filled with gas to a pressure of 50 cm of Hg for measurements on weaker bands and another 10 cm long filled with gas to 10 cm Hg pressure for measurements on the more intense regions of absorption.

A set of preliminary measurements extending from 1.0μ to 13.0μ was made with a prism spectrometer of the Wadsworth type, to determine the approximate positions of the principal regions of absorption and their relative intensities. Four fairly intense regions were found, enumerated in the order of their intensities at 4.74μ, 10.7μ, 3.4μ, and 2.3μ. A much weaker peak was found near 5.7μ. Of these the three regions at 3.4μ, 4.74μ and 10.7μ have been studied under high dispersion using a prism grating spectrometer described in relation to earlier experiments, and two different echellette gratings ruled by Wood, one with 4800 lines to the inch for the 4.0μ region and another with 800 lines to the inch for the 10μ region.

[1] A. H. Nielsen and H. H. Nielsen, Phys. Rev. **48**, 864 (1935).
[2] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 828 (1935).

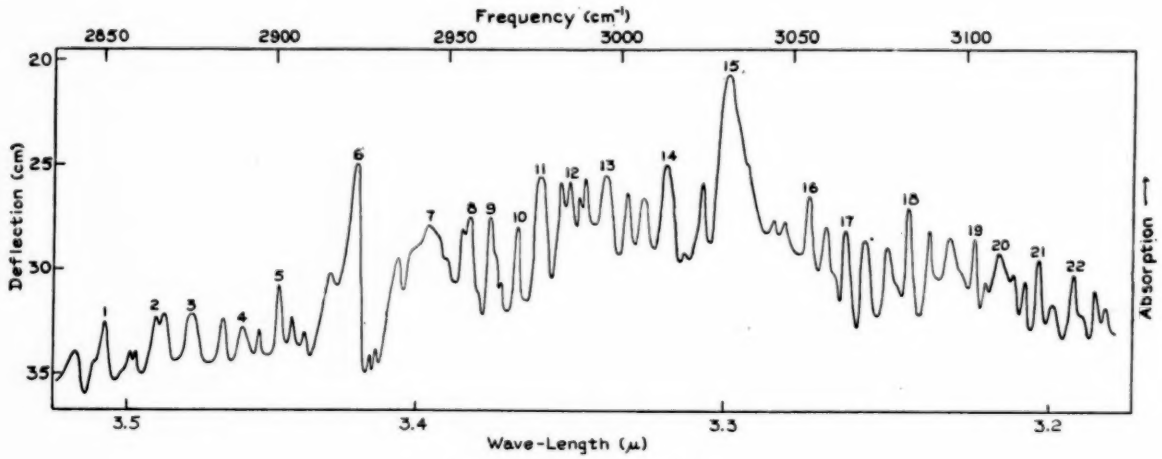

FIG. 1. 3.3μ region of GeH_4.

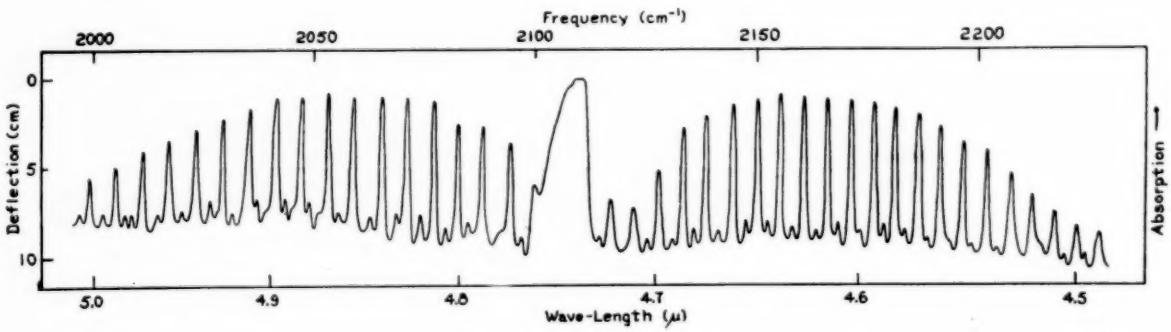

FIG. 2. 4.7μ band of GeH_4.

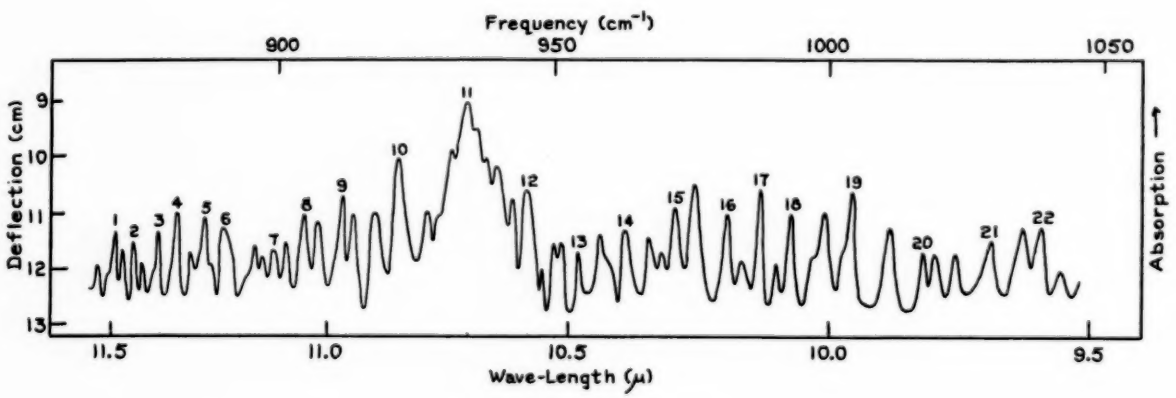

FIG. 3. 10.7μ region of GeH_4.

In these regions, spectrometer slits equivalent to frequency intervals in the spectrum of 0.8 cm^{-1}, 0.8 cm^{-1} and 0.6 cm^{-1}, respectively, could be used and galvanometer deflections were taken at divisions on the circle equal to the spectral range subtended by the spectrometer slit in each case. Moreover, all three of these regions are quite free from lines of atmospheric absorption so that the data have been recorded throughout in terms of galvanometer deflections. The absorption patterns for these regions obtained by plotting galvanometer deflections as ordinates

TABLE I. *3.3μ region of GeH_4.*

LINE No.	FREQ. (cm^{-1})	LINE No.	FREQ. (cm^{-1})	LINE No.	FREQ. (cm^{-1})
	2841.6	8	2956.7	17	3065.8
1	2850.3	9	2962.8		3071.8
2	2864.8	10	2970.1		3078.1
	2868.0	11	2977.2	18	3084.3
3	2875.7		2983.7		3090.0
	2885.0	12	2986.0		3095.8
4	2890.0		2990.2	19	3102.8
	2894.9	13	2996.1	20	3109.2
5	2901.1		3002.0		3113.7
	2905.0		3006.8		3117.6
	2908.3	14	3013.4	21	3121.5
	2915.1		3023.7		3126.0
6	2922.7	15	3031.0	22	3131.9
	2936.0	16	3054.9		3138.3
7	2945.5		3059.9		3141.0

TABLE II. *4.7μ region of GeH_4.*

LINE No	FREQ. (cm^{-1})	LINE No.	FREQ. (cm^{-1})	LINE No.	FREQ. (cm^{-1})
1	1998.9	15	2082.7	29	2166.1
2	2005.1	16	2088.4	30	2171.3
3	2011.7	17	2094.3	31	2176.5
4	2017.5	18	2099.8	32	2181.8
5	2023.3	19	2110.1	33	2187.1
6	2029.4	20	2116.8	34	2192.0
7	2035.3	21	2122.4	35	2197.1
8	2041.4	22	2128.0	36	2202.4
9	2047.5	23	2133.6	37	2207.1
10	2053.4	24	2138.9	38	2212.2
11	2059.3	25	2144.6	39	2217.0
12	2065.1	26	2150.0	40	2222.1
13	2071.2	27	2155.1	41	2226.9
14	2077.1	28	2160.9		

TABLE III. *10.7μ region of GeH_4.*

LINE No.	FREQ. (cm^{-1})	LINE No.	FREQ. (cm^{-1})	LINE No.	FREQ. (cm^{-1})
1	870.0		913.5	16	981.1
	871.3		917.1		983.5
2	873.3	10	921.4	17	986.9
	875.2		926.6		990.2
3	877.9	11	934.0	18	992.8
4	881.2	12	944.5		998.7
	883.8		949.9	19	1004.7
5	885.8		951.5		1010.8
6	889.2	13	954.6	20	1017.0
7	898.4		958.5		1018.8
	901.1	14	963.2		1022.4
8	904.3		967.2	21	1028.7
	906.8	15	971.7		1034.2
9	912.1		974.9	22	1037.9

against a scale of frequencies and wave-lengths are given in Figs. 1, 2 and 3 and accompanying each figure is a tabulation of frequencies of the principal lines (Tables I–III).

The region near 3.3μ apparently corresponds to the 2.3μ region in the methane spectrum and the 3.2μ region in the silane spectrum, and like these it consists of two badly overlapping bands with centers at 2922.7 cm^{-1} and 3031.0 cm^{-1}. By analogy to the spectra of methane and silane these two bands have been identified as $\nu_1+\nu_4$ and $\nu_3+\nu_4$, respectively. Because of the overlapping, it is impossible to find any regularity of line spacing except perhaps on the high frequency side of the band at 3031 cm^{-1} where an average over several nearly equally spaced lines leads to a value of 6.2 cm^{-1} for the separation between lines.

The 4.7μ band with its center at 2110 cm^{-1} undoubtedly corresponds to the 3.3μ band in the methane spectrum and the 4.5μ band in the silane spectrum and is accordingly designated as ν_3. It is the most intense of the bands measured in the germane spectrum. Like the corresponding bands in the spectra of methane and silane, it consists of a strong central line with a series of sharp rotation lines on either side forming *P* and *R* branches. As may be seen from Fig. 3, there occurs also here a background which we do not believe can be ascribed to observational errors since it has been repeated almost exactly a number of times. The background is here not as predominant as in the corresponding band in the silane spectrum and neither is the *Q* branch so extremely broad, so that as a whole this region resembles the corresponding one in the methane spectrum a great deal more than that in the silane spectrum. Some convergence of the principal lines is observed towards higher frequencies and the average separation between lines taken over the entire band is found to be 5.56 cm^{-1}.

The long wave-length region has its center at 934 cm^{-1} and is taken to correspond to the 7.7μ band in the methane spectrum and to the 9.5μ band in the silane spectrum. It is consequently identified as ν_4. It should be pointed out that while the high frequency fundamentals in the methane and silane spectra appear to be less intense than the low frequency fundamentals, the opposite is here true, but aside from this the 10.5μ region in the germane spectrum resembles the 7.7μ methane band a great deal, in fact much more so than the corresponding silane band which occurs as two overlapping bands. While here as in methane some regularity of rotationa

structure is discernible, especially on the high frequency side where a separation of about 6.0 cm^{-1} seems to establish itself, the structure is quite definitely not the simple structure to be expected for so symmetrical a molecule.

It is felt that these measurements as well as the earlier ones on methane and silane emphasize the importance of remeasuring the bands of all the X-tetrahydrides (XH_4) at much reduced temperatures, to establish whether the complex structure observed in many cases can be ascribed to overlapping bands arising from transitions between higher vibration levels or whether a more involved explanation is to be sought. We hope soon to be able to report on such measurements.

When the spacings in the two optically active fundamentals vibrations ν_3 and ν_4 have been determined, it is possible by the method of Dennison and Johnston[3] to compute the value for the moment of inertia of the molecule. This we have done also for the germane molecule taking the spacings between lines in the two fundamentals ν_3 and ν_4 to be 5.6 cm^{-1} and 6.0 cm^{-1}, respectively. These spacings lead to a value for the moment of inertia of the germane molecule of 7.0×10^{-40} g-cm^2 and to the values 1.37×10^{-8} and 2.06×10^{-8} cm for the Ge-H and the H-H distances. It must be emphasized that the structure of ν_4 is so irregular and its spacing constant so doubtful that the above values are highly uncertain.

[3] D. M. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935).

TABLE IV. *Summary of assignments of the absorption bands of germane.*

OBSERVED ν	COMPUTED ν	IDENTIFICATION
—	820 cm^{-1}	ν_2
934.cm^{-1}	—	ν_4
1754	—	$\nu_2+\nu_4$ (?)
—	1988.7	ν_1
2110.1	—	ν_3
2922.7	—	$\nu_1+\nu_4$
3031.0	3044.1	$\nu_3+\nu_4$
4250	4220.2	$2\nu_3$.

For convenience we have restated in Table IV our identification of the bands observed in the spectrum of germane.

We wish to express our gratitude to Professor Warren C. Johnston for the sample of germane gas which he so kindly presented to us.

DECEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

The Infrared Absorption Bands of Methane

ALVIN H. NIELSEN* AND HARALD H. NIELSEN, *Mendenhall Laboratory of Physics, Ohio State University*

(Received September 30, 1935)

The two fundamental vibration-rotation bands ν_3 and ν_4 of methane have been remeasured with greater resolution than that available in the earlier investigation of Cooley. Whereas the band at 3.3μ showed no essentially new details, the fundamental band at 7.7μ was found to possess a somewhat more complex rotational structure than was observed by Cooley. Many of the lines given in Cooley's curve are here resolved into groups of closely spaced components. The separation between the components within a group appears to increase with the ordinal number of the line counted outward from the center of the band. In addition to these measurements, the two combination bands $\nu_1+\nu_4$ at 4218 cm^{-1} and $\nu_3+\nu_4$ at 4315 cm^{-1} have been at least partially resolved and appear to have line spacings of about 5.3 cm^{-1} and 13.5 cm^{-1}, respectively.

RECENT measurements on the absorption spectrum of silane[1] in the infrared have shown that the rotation lines are not single sharp lines, but are accompanied by satellite components. Because of the apparent similarity between the methane and silane molecules it has seemed worth while to remeasure the known absorption bands in methane under the improved conditions made available since the investigation by Cooley[2] was made.

* Honorary Fellow in Physics, Ohio State University.

[1] W. B. Steward and H. H. Nielsen, J. Chem. Phys. **2**, 712 (1934); Phys. Rev. **47**, 828 (1935).

[2] J. P. Cooley, Astrophys. J. **62**, 73 (1925).

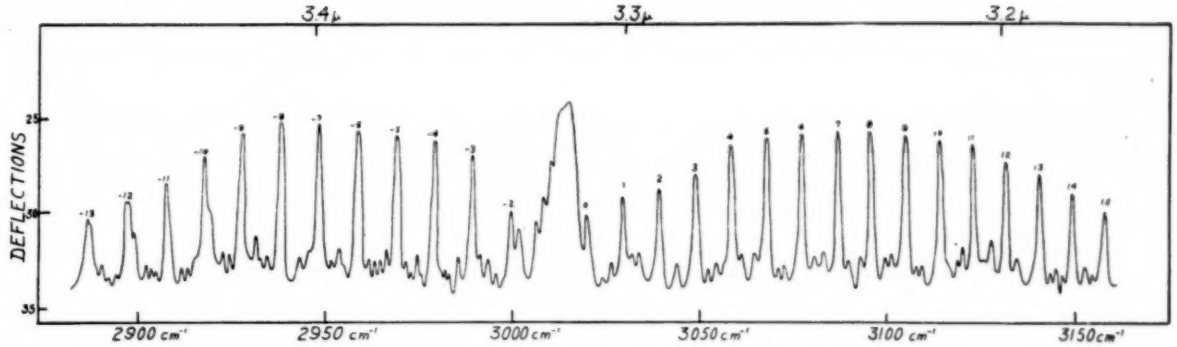

FIG. 1. Absorption pattern of methane in the 3.3μ region.

For the measurements reported here, a prism-grating spectrometer with a collimating mirror of two-meter focal length was used. There were available three echelette gratings ruled by R. W. Wood, one with 3600 lines per inch for the 3.5μ region, one with 4800 lines per inch used in second order for the 2.3μ region, and one with 2000 lines per inch for the 7.0μ region. The methane gas was prepared by dropping distilled water on chemically pure aluminum carbide. To guard further against impurities the gas was fractionally distilled into the evacuated absorption cells to atmospheric pressure. For the 3.3μ and 7.7μ bands a cell of 2 cm length was used, and for the 2.3μ bands the cell was 6 cm in length. These cells were fitted with windows of polished rocksalt.

THE 3.3μ REGION

The 3.3μ fundamental band of methane, ν_3, is shown in Fig. 1. The curve is plotted in galvanometer deflections against a scale of frequencies in cm^{-1} and a scale of wave-lengths in μ. The band, while here completely resolved, reveals nothing essentially different from the earlier curve of Cooley except for the very weak background observable between the lines in Fig. 1. Concerning this background it must be said that while it can be reproduced in detail and can in no way be ascribed to observational errors, it is difficult to identify it definitely as a part of the methane spectrum since there is in this region a small amount of atmospheric water vapor absorption. Measurements have, however, been made on this band with the cell in the beam and with the cell out of the beam, and when the data were plotted as percent absorption this same background persisted. It was also found impossible to make any correlation whatever between the background and the fluctuation of the deflections due to atmospheric absorption. The slit widths used for measurement in this region included about 0.8 cm^{-1} and galvanometer deflections were read at intervals of about 0.8 cm^{-1}. Table I gives the new frequency and wave-length positions of the lines in the band, and numbers corresponding to those in Cooley's curve have been assigned.

TABLE I. *The frequencies and wave-lengths of the lines in the 3.3μ band of methane.*

LINE NO.	FREQ. (cm^{-1})	WAVE-LENGTH (μ)	LINE NO.	FREQ. (cm^{-1})	WAVE-LENGTH (μ)
−13	2886.1	3.4649	+2	3039.0	3.2906
−12	2896.7	3.4522	+3	3048.6	3.2802
−11	2907.0	3.4400	+4	3058.1	3.2700
−10	2917.7	3.4274	+5	3067.5	3.2600
−9	2927.8	3.4155	+6	3077.0	3.2499
−8	2938.1	3.4036	+7	3086.3	3.2401
−7	2948.3	3.3918	+8	3095.4	3.2306
−6	2958.6	3.3800	+9	3104.7	3.2209
−5	2968.8	3.3684	+10	3113.6	3.2117
−4	2979.1	3.3567	+11	3122.6	3.2025
−3	2989.2	3.3454	+12	3131.6	3.1933
−2	2999.7	3.3367	+13	3140.3	3.1844
0	3019.6	3.3117	+14	3149.2	3.1754
+1	3029.1	3.3013	+15	3157.8	3.1668

THE 7.7μ REGION

In Fig. 2 we reproduce ν_4, the 7.7μ fundamental of methane as given by our measurements. This curve is plotted in percent absorption against a scale of frequencies in cm^{-1} and wave-lengths in μ, readings having been taken with the cell in the beam and with the cell out of the beam to compensate for any atmospheric lines in this region. Galvanometer deflections were

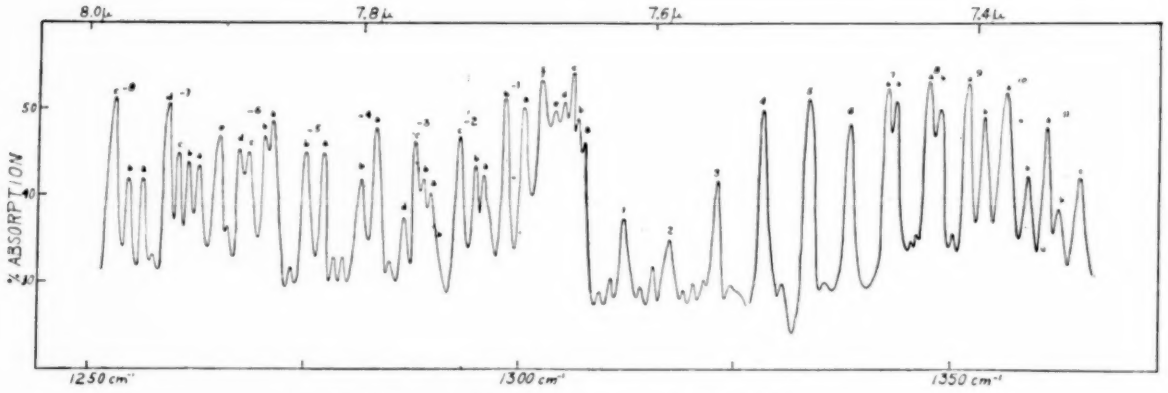

FIG. 2. Absorption pattern of methane in the 7.7μ region.

read at intervals of about 0.4 cm^{-1} and the slits included about 0.45 cm^{-1}. Several of the lines, however, were studied separately with somewhat narrower slits and with the readings taken at correspondingly smaller intervals. Cooley's curve quite definitely suggests a more complex structure, and this is just what is shown by our measurements in Fig. 2. The nature of the effect is best seen in the high frequency side of the band, the low frequency side being further distorted by the very broad Q branch which here is apparently partially resolved. On the high frequency side no essential difference between Cooley's curve and Fig. 2 is observed until the seventh line which we have resolved into two components lying 0.8 cm^{-1} apart. The components of the following lines are successively more widely separated. It is difficult to compare Cooley's curve with Fig. 2 on the low frequency side since Cooley's curve extends only to the fifth line. It will be seen, however, that the positions in our curve corresponding to lines -2, -3, -4 and -5 contain 3, 4, 2 and 2 components, respectively, some of which are probably due to the resolved structure of the very broad Q branch. Table II gives the frequency and wave-length positions of the lines in the band numbered as in Cooley's work except that the components of the lines have been given the assignments a, b, c, etc.

THE 2.3μ REGION

The combination bands $\nu_1+\nu_4$ and $\nu_3+\nu_4$ at 2.3μ, at least partially resolved, are shown in Fig. 3. It will be remembered that none of the fine structure of these bands was resolved in the earlier work. The curve in Fig. 3 is plotted in galvanometer deflections against a scale of frequencies in cm^{-1} and wave-lengths in μ, the deflections having been read at intervals of 0.9 cm^{-1} by using slit widths which included about 0.8 cm^{-1}. With the Q branches separated by only 97 cm^{-1} the R branch of $\nu_1+\nu_4$ and the P branch of $\nu_3+\nu_4$ overlap to such an extent that no estimate of the line spacings of these bands

TABLE II. *The frequencies and wave-lengths of the lines in the 7.7μ band of methane.*

LINE No.	FREQ. (cm^{-1})	WAVE-LENGTH (μ)	LINE No.	FREQ. (cm^{-1})	WAVE-LENGTH (μ)
-8 c	1253.0	7.9808	f	1302.4	7.6781
b	1254.4	7.9719	e	1304.1	7.6681
a	1256.1	7.9612	d	1305.1	7.6622
-7 d	1259.1	7.9422	c	1306.1	7.6564
c	1260.3	7.9346	b	1306.8	7.6523
b	1261.5	7.9271	a	1307.6	7.6476
a	1262.6	7.9202			
-6 e	1265.2	7.9039	1	1312.2	7.6207
d	1267.4	7.8902	2	1317.5	7.5901
c	1268.5	7.8833	3	1322.9	7.5591
b	1270.3	7.8722	4	1328.1	7.5295
a	1271.1	7.8672	5	1333.3	7.5001
-5 b	1275.1	7.8431	6	1338.2	7.4727
a	1277.3	7.8290	7 a	1342.7	7.4476
-4 d	1278.4	7.8223	b	1343.5	7.4432
c	1279.5	7.8156	8 a	1347.4	7.4217
b	1281.7	7.8021	b	1348.7	7.4145
a	1283.1	7.7936	9 a	1352.0	7.3964
-3 d	1286.6	7.7724	b	1353.7	7.3871
c	1287.7	7.7658	10 a	1356.4	7.3724
b	1288.7	7.7598	b	1358.9	7.3752
a	1289.6	7.7543	11 a	1360.8	7.3484
-2 c	1293.0	7.7340	b	1362.3	7.3404
b	1294.9	7.7226	c	1364.9	7.3261
a	1295.7	7.7184			
-1 b	1298.1	7.7036			
a	1300.3	7.6905			

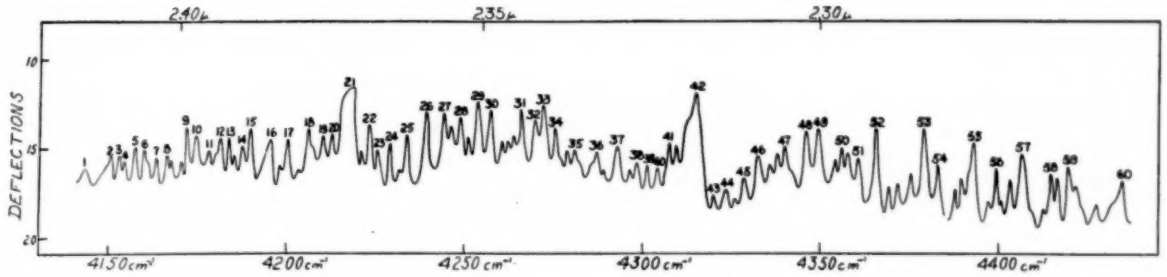

FIG. 3. Absorption pattern of methane in the 2.3μ region.

can be made from this region. However, certain lines stand out more prominently than others in the P branch of $\nu_1+\nu_4$ and the R branch of $\nu_3+\nu_4$ and it seems reasonable to assign a spacing of about 5.3 cm^{-1} and 13.5 cm^{-1} to these two bands, respectively. Table III gives the frequencies in cm^{-1} and the wave-lengths in μ of the lines resolved in this region. For identification arbitrary numbers have been assigned to the lines in the two bands.

TABLE III. *The frequencies and wave-lengths of the lines in the 2.3μ bands of methane.*

LINE No.	FREQ. (cm^{-1})	WAVE-LENGTH (μ)	LINE No.	FREQ. (cm^{-1})	WAVE-LENGTH (μ)
1	4143.4	2.4135	31	4265.8	2.3442
2	4150.4	2.4094	32	4269.9	2.3420
3	4152.8	2.4080	33	4272.0	2.3408
4	4154.4	2.4071	34	4275.4	2.3390
5	4157.1	2.4055	35	4280.8	2.3360
6	4159.9	2.4039	36	4287.2	2.3325
7	4163.0	2.4021	37	4293.1	2.3293
8	4166.2	2.4003	38	4298.2	2.3266
9	4171.7	2.3971	39	4301.6	2.3247
10	4174.5	2.3955	40	4304.1	2.3234
11	4178.1	2.3934	41	4307.5	2.3215
12	4181.3	2.3916	42	4314.4	2.3178
13	4183.7	2.3902	43	4320.4	2.3146
14	4187.7	2.3879	44	4323.8	2.3128
15	4189.7	2.3868	45	4328.5	2.3103
16	4195.7	2.3834	46	4332.4	2.3081
17	4200.5	2.3807	47	4339.6	2.3044
18	4206.2	2.3774	48	4345.9	2.3010
19	4210.2	2.3752	49	4349.1	2.2993
20	4212.9	2.3737	50	4355.9	2.2957
21	4217.5	2.3710	51	4360.5	2.2933
22	4223.2	2.3679	52	4365.6	2.2906
23	4225.7	2.3665	53	4378.8	2.2837
24	4229.4	2.3644	54	4382.8	2.2816
25	4233.9	2.3619	55	4393.0	2.2763
26	4239.2	2.3589	56	4399.2	2.2731
27	4244.2	2.3562	57	4406.4	2.2694
28	4248.7	2.3537	58	4414.5	2.2653
29	4253.7	2.3509	59	4419.5	2.2627
30	4257.4	2.3489	60	4429.9	2.2574

DISCUSSION OF EXPERIMENTAL RESULTS

We do not, in this communication, propose to give any adequate explanation for the complex structure observed at 7.7μ. The possibility suggests itself that it may be due to upper stage bands; i.e., to transitions between higher vibration states. It would, however, seem unlikely that these would be observed as anything but second-order effects in this region of the spectrum. Another explanation is the one suggested in connection with a similar effect observed in silane, that this structure is in some way intimately associated with the convergence of the lines in the bands. This issue can only be definitely settled, as was earlier suggested, by remeasuring the bands with the gas at greatly reduced temperatures. This we hope to do in connection with similar measurements on the bands of silane and germane.

May we take this opportunity to express our appreciation of a gift from the International Salt Company of Scranton, Pennsylvania, of several pieces of optical rocksalt used in making windows for our absorption cells. A grant-in-aid from the National Research Council is also acknowledged with gratitude.

The Interaction Between Vibration and Rotation for Symmetrical Molecules

MANFRED JOHNSTON AND DAVID M. DENNISON, *University of Michigan*

(Received September 14, 1935)

The explanation first proposed by Teller of the anomalous fine structure of the infrared bands of symmetrical molecules is discussed. The fine structure is closely related to an internal angular momentum of magnitude $\zeta h/2\pi$ which is due to the vibration of the molecule and arises from the degenerate character of the motion. A simple derivation is given for the spacing constant $[(1-\zeta)/C-1/A]h/4\pi^2$ of axially symmetric molecules and for the spacing constant $(1-\zeta)h/4\pi^2A$ of tetrahedral molecules. A detailed calculation is made of the internal angular momenta to be associated with the $\perp$ frequencies ν_2 and ν_4 of the axial molecule YX_3. The resulting ζ's are found as functions of the moments of inertia and of the potential constants. The sum $\zeta_2+\zeta_4$ is shown to have the value $C/2A-1$. These results are applied to the molecules NH_3 and ND_3 and the line spacings of ν_2 and ν_4 are computed. The axial molecule ZYX_3 is treated and it is proved that the sum of the ζ's characterizing the three $\perp$ bands ν_2, ν_4, and ν_6 is equal to $C/2A$. The moment of inertia C of the methyl halides is computed and found to be, 5.61, 5.35, 5.44, and 5.44×10^{-40} for methyl fluoride to methyl iodide, respectively. The error is estimated to be around 5 percent. A calculation is made of the ζ's to be associated with the overtones of axial molecules possessing threefold symmetry. It is found that the ζ appropriate for the overtone $2\nu_i$ of a $\perp$ frequency is $-2\zeta_i$ while the ζ for $3\nu_i$ is ζ_i itself. The combination of two $\perp$ frequencies $\nu_2+\nu_4$ is next treated and the ζ is proved to be $-(\zeta_2+\zeta_4)=1-C/2A$. An application of these formulae to the observed spacings of the overtone bands of NH_3 and CH_3Cl results in a very satisfactory agreement. Expressions are obtained for the two ζ's which determine the line spacings of the active fundamentals ν_3 and ν_4 of the tetrahedral molecule YX_4. It is shown that $\zeta_3+\zeta_4=\frac{1}{2}$. The positions of the fundamental bands of methane together with the line spacings of ν_3 and ν_4 yield the moment of inertia $A=5.47\times10^{-40}$ together with the five potential constants describing the molecule. A good agreement is found between these constants and those obtained by Ginsburg and Barker from the spectrum of methyl deuteride. The ζ's suitable for the overtones of YX_4 are next treated. It is found that the ζ to be used with $2\nu_i$, $i=3, 4$ is $-\zeta_i$ while the ζ belonging with the combination band $\nu_3+\nu_4$ is $-\frac{1}{2}(\zeta_3+\zeta_4)=-\frac{1}{4}$. The observations on the overtones of methane are in very good accord with these expressions. Less satisfactory agreement is obtained in the case of the silane spectrum where it appears that the higher order perturbation terms play a larger role.

§1. INTRODUCTION

DURING the past several years, great progress has been made in interpreting the spectra of polyatomic molecules. The molecule has been represented by a system of mass points whose equilibrium positions constitute the configuration of the molecule. It is assumed that, in zeroth approximation, the mass points are bound by elastic forces and that throughout their vibratory motion they remain essentially in the neighborhood of their equilibrium configuration. From this model it has been possible to understand the spectra of many molecules and to compute such physical constants as the potential energy function and the dimensions of the system. However, one grave difficulty has appeared in that the simple theory predicts that for a given molecule all the infrared bands which correspond to a particular type of vibration should show the same fine structure. This prediction is fulfilled for many types of vibration, for example, the $\parallel$ bands of ammonia. However, it is flagrantly violated for others, notably the bands of methane and the $\perp$ bands of the methyl halides.

A solution to this problem has recently been given by Teller[1] who has pointed out that those vibrations which show anomalous fine structure are degenerate and may possess an angular momentum arising from the vibratory motion itself. The interaction between this angular momentum and that due to the rotation of the molecule will just account for the observed effects. The purpose of the present paper is to extend Teller's theory and to make detailed calculations for several molecular models.

The algebra involved in the computations is often rather complicated and may hide the simplicity of the underlying ideas. The vibratory motion of the nuclei may be regarded as a motion taking place on a slowly rotating turntable corresponding to the rotation of the molecule. This rotation of the system introduces a Coriolis force into the vibrational motion which in turn makes a contribution to the energy. In general, the con-

[1] E. Teller, *Hand- und Jahrbuch d. chem. Physik* (1934), Vol. 9, p. 125.

tribution is very small (of second order) since the motion of each particle relative to the turntable is, to a high approximation, simple harmonic motion along a straight line. Thus the average Coriolis force is zero. However, for a degenerate vibration, which corresponds to the existence of two or more harmonic motions of equal frequency at right angles to each other, this is by no means the case. A suitable choice of amplitudes and phases renders the motion for each particle circular or at least elliptical. Here the average Coriolis force does not vanish but has the value $\pm k\omega$ where k is a proportionality factor and ω is the angular velocity of the turntable. The plus and minus signs relate to whether or not the circular motion of vibration is in the same direction as the rotation of the turntable. We shall now compute in detail the first order change in energy caused by the rotation.

It is convenient to introduce a moving coordinate system x, y, z whose axes are defined by the equilibrium positions of the nuclei and which coincide with the principal axes of inertia A, B, C. If the molecule possesses degenerate frequencies, there will be in general an angular momentum produced by the vibrational motion itself. The components of this internal angular momentum p, along the axes x, y, z will be designated by p_x, p_y, p_z. The eigenvalues of the internal angular momentum are not necessarily integral multiples of $h/2\pi$ since p relates to only part of the system, namely, the vibration, and does not take account of the rotation of the molecule. Following Teller we shall introduce ζ as the proportionality factor. In molecules having an axis of symmetry, such as the methyl halides, ammonia, etc., p lies along this axis and has the magnitude $\zeta h/2\pi$. For molecules having tetrahedral symmetry (methane) the vibrations in which we are interested possess spherical symmetry and consequently,

$$p^2=l(l+1)\zeta^2h^2/4\pi^2.$$

The quantity ζ is essentially dependent upon the vibrational properties of the molecule, that is, upon the relative dimensions, the masses, and the force constants. It has different values for the various normal modes of vibration. For this reason the individual bands of the same molecule may show different fine structure spacings. A knowledge of the ζ's as determined from the fine structure enables us to obtain information regarding the force constants of the molecule.

It is now necessary to consider the total angular momentum of the molecule P which includes the contributions due to the rotation and to the vibration. It has the components P_x, P_y, P_z along the moving axes and must be quantized. The formula for the rotational energy of a rotator involving an internal flywheel has appeared many times in the literature and has the form,

$$H_{\text{rot}}=(P_x-p_x)^2/2A+(P_y-p_y)^2/2B+(P_z-p_z)^2/2C.$$

This expression has recently been carefully reexamined by Eckart,[2] Van Vleck,[3] and others, and appears to be entirely correct.

The rotational energy levels of the symmetric rotator, $A=B$, C may be readily obtained. The internal angular momentum for such a molecule must lie along the symmetry axis C and hence $p_x=p_y=0$ and $p_z=\pm p$, the double sign indicating whether p is parallel or antiparallel to the C axis. We may write the rotational energy

$$H_{\text{rot}}=(P_x^2+P_y^2+P_z^2)/2A+P_z^2(1/2C-1/2A)\mp pP_z/C+p^2/2C.$$

The Hamiltonian may be diagonalized by using the representation for P such that P_z has only diagonal elements. $P_z=Kh/2\pi$ where K is a positive or negative integer. The total angular momentum is of course diagonal.

$$P_x^2+P_y^2+P_z^2=J(J+1)h^2/4\pi^2.$$

Hence

$$W_{\text{rot}}=J(J+1)h^2/8\pi^2A+(1/C-1/A)K^2h^2/8\pi^2\mp\zeta Kh^2/4\pi^2C.$$

The last term $p^2/2C$ may be omitted since it does not depend upon the rotation and hence may be absorbed into the vibrational energy.

In order to find the actual frequencies of the fine structure lines we must make use of the selection rules. These may be obtained by the rather laborious process of examining the matrix elements of the electric moment. However, they

[2] C. Eckart, Phys. Rev. **47**, 552 (1935).
[3] J. H. Van Vleck, Phys. Rev. **47**, 487 (1935).

may be easily understood from the following argument. The electric moment depends upon the positions of the nuclei. In the coordinate system x, y, z which moves with the molecule, the electric moment executes circular motion about the axis of symmetry. Suppose that the direction of rotation of the electric moment is in the same sense as the direction of the angular momentum of vibration p. Now if p and P_z are in the same sense (in which case we use the upper or minus sign in the expression for W_{rot}) the motion of the electric moment may be described as a rotation about the symmetry axis with a frequency $\nu_0+\nu_K$ and a precession about the P axis with a frequency ν_J. Thus, if the vibrational quantum number goes from $0\rightarrow 1$ we have $K\rightarrow K+1$ and $J\rightarrow J-1$, $J\rightarrow J+1$, or $J\rightarrow J$ as the possible transitions. In the case where p and P_z are in opposite senses, the frequency of rotation is clearly $\nu_0-\nu_K$ and the selection rules are, vibrational number $0\rightarrow 1$, $K\rightarrow K-1$ and $J\rightarrow J-1$, $J\rightarrow J+1$, or $J\rightarrow J$. We must here use the plus sign in W_{rot}.

In the $\perp$ bands of axial molecules it usually happens that only the so-called zero-branch lines for which $J\rightarrow J$ are observed. The frequency of the fine structure lines under *either* of the above sets of rules (p parallel or antiparallel to P_z) is then

$$\nu=\nu_0-(1/C-1/A)h/8\pi^2 +[(1-\zeta)/C-1/A]Kh/4\pi^2, \qquad K=0,\ \pm 1,\ \pm 2,\ \cdots.$$

In deriving this formula it was assumed that the direction of rotation of the electric moment was parallel to the angular momentum p. However, it may occur that the rotation of the electric moment and the internal angular momentum are antiparallel. In this case the selection rules are just reversed and the spacing of the zero-branch lines may be shown to be $[(1+\zeta)/C-1/A]\times(h/4\pi^2)$. It is convenient to retain only the first formula and to consider that ζ is positive or negative according to whether the rotation of the electric moment and the vibrational angular momentum have the same or opposite senses.

Finally it must be remarked that we have here considered a transition from the normal state, where there is no vibrational angular momentum, and consequently $\zeta=0$, to an excited state $\zeta=\zeta$. These bands are the ones most frequently observed experimentally. However, transitions may occur between two excited levels, each of which has a ζ different from zero. In this case the above formula for the fine structure lines would be altered.

The second class of molecules to be treated in this paper is the group of molecules which have tetrahedral symmetry. For these all three moments of inertia are the same. The Hamiltonian may be written in the simple form

$$H_{\text{rot}}=P^2/2A-(P\cdot p)/A+p^2/2A.$$

The first term becomes $J(J+1)h^2/8\pi^2A$ in virtue of the diagonal nature of the total angular momentum P^2, while the third term may be absorbed into the vibrational energy. The second term, which contains the scalar product of the total angular momentum P and the internal angular momentum p, represents the interaction which we wish to evaluate.

The fundamental frequencies of the methane molecule which are active in the infrared are to be associated with a transition from the normal state where there is no internal angular momentum to the first excited state of a three-dimensional isotropic oscillator. This latter state possesses an internal angular momentum p which may have the three eigenvalues $\pm\zeta h/2\pi$ and 0. Thus the interaction term I may be written $I=-(\Pi\cdot\pi)\zeta h^2/4\pi^2A$ where Π is a vector having eigenvalues $J, J-1, \cdots -J$ and π has the values 1, 0, -1. The expression for the eigenvalues of $(\Pi\cdot\pi)$ is well known in spectroscopy and is

$$2(\Pi\cdot\pi)=J(J+1)+2-R(R+1).$$

R is a vector which, when compounded with π, will give the total momentum Π. Evidently it may take on the values $J-1$, J, and $J+1$ thus yielding the following three eigenvalues for $(\Pi\cdot\pi)$; $J+1$, 1, and $-J$. Now the vector R corresponds to a rotation of the molecular framework and the three values for $(\Pi\cdot\pi)$ are to be correlated with the three possibilities, p parallel to P, p perpendicular to P, and p antiparallel to P, respectively. These considerations furnish a key to the selection rules and show that in making a transition from the normal to the excited

state we must use the first, second, or third eigenvalue of $(\Pi \cdot \pi)$ according as $J-1 \rightarrow J$, $J \rightarrow J$, or $J \rightarrow J-1$. We thus obtain the following formulae for the fine structure lines

Positive branch $J-1 \rightarrow J$ $\quad \nu = \nu_0 - h\zeta/4\pi^2 A + Jh(1-\zeta)/4\pi^2 A$

Zero branch $J \rightarrow J$ $\quad \nu = \nu_0 - h\zeta/4\pi^2 A$

Negative branch $J \rightarrow J-1$. $\quad \nu = \nu_0 - h\zeta/4\pi^2 A - Jh(1-\zeta)/4\pi^2 A$.

It thus appears that the form of the vibration-rotation bands has not been changed by the introduction of an internal angular momentum. However the actual spacing of the fine structure lines is altered by the factor $(1-\zeta)$. These results, which have also been obtained by Teller, we believe to be correct only up to the first-order approximation here treated. In higher approximation where the particular symmetry of the molecule must be taken into account it seems probable that the fine structure lines will be divided into multiplets.[4] It is hoped shortly to make calculations on this effect of which there are already some experimental indications.

The formulae which have been developed show that the line spacing depends essentially upon a quantity ζ without a knowledge of which the experimental data cannot be interpreted. $\zeta h/2\pi$ represents the angular momentum due to the vibratory motion of the nuclei relative to a coordinate system defined by the equilibrium positions of the nuclei. This internal angular momentum may always be computed as a function of the force constants, the masses, and the relative dimensions of the molecule, but in many cases the actual calculation becomes very laborious and involved. There exists, however, an important theorem discovered by Teller[1] which states that the sum of the ζ's of all the first excited states belonging to a given symmetry class is independent of the force constants and is a function only of the masses and the relative dimensions of the molecule. The quantity $\Sigma\zeta$ is thus relatively simple to compute since in making the calculation we may use any type of force field, in particular, such forces that the motion of the system may be readily visualized. Immediate use may be made of $\Sigma\zeta$ since the sum of the fine structure spacings of all the fundamental bands of a given category depends only upon $\Sigma\zeta$ and not upon the individual ζ's. This point will be illustrated later in the present paper.

[4] See the concluding portion of the present paper.

§2. Axially Symmetric Molecules

We begin our discussion of molecules having an axis of symmetry by considering the system YX_3, of which ammonia is a representative. It is well known that the regular pyramid YX_3 possesses four normal frequencies which are separated into two symmetry classes, the two $\parallel$ frequencies and the two $\perp$ frequencies. Since these belong to different symmetry classes the Hamiltonian falls into two parts and there exist no interaction terms. It is only the $\perp$ frequencies which are degenerate and which may exhibit an internal angular momentum. Consequently we shall treat them exclusively in what follows. In separating the $\parallel$ and $\perp$ vibrations it is only necessary to introduce symmetry coordinates; coordinates which are capable of specifying all possible configurations of the system which belong to the desired symmetry class.

We shall begin by obtaining the kinetic energy and we will make use of the theorem that the kinetic energy of any system may be regarded as the sum of two terms, the energy relative to the center of gravity of the system and the translational energy of the center of gravity. We shall divide the YX_3 molecule into two parts, the Y atom and the X_3 group. The energy may thus be written as the energy of the Y atom, the translational energy of the center of gravity of the X_3 group and the energy of the X_3 group relative to its center of gravity. The method of calculation is made clearer by Fig. 1. The dotted horizontal line is the equilibrium position of the figure axis. The center of gravity of the X atoms is shown by the letter G and the quantity y_1 is the sum of the displacements of the Y atom and G. The inclination of the plane of the X atoms to the symmetry line is indicated by the angle θ.

The kinetic energy of the whole system is then

$$T = \tfrac{1}{2}\mu\dot{y}_1^2 + \tfrac{1}{2}I\dot{\theta}^2 + T_0,$$

where μ is the reduced mass of the Y atom and G, that is, $\mu = 3mM/(3m+M)$; m and M being the masses of the X and Y atoms, respectively. The

second term represents the energy of tipping of the X_3 triangle and I is the moment of inertia of the triangle about an axis through G lying in the plane of the triangle. It will be more convenient to use the substitution $I=C/2$ where C is the moment of inertia of the X_3 atoms, and hence of the whole YX_3 molecule about the figure axis. T_0 denotes the kinetic energy of the X atoms within their plane and relative to G. We shall presently evaluate T_0; the only point to consider for the instant is that there can be no interaction terms between T_0 and the tipping term $\frac{1}{2}I\dot{\theta}^2$ since the displacements of the particles for the two motions are always perpendicular.

The first two terms of T may be combined because of the condition that the angular momentum of the system perpendicular to the symmetry axis must remain zero throughout the motion. (This is equivalent to the demand, explained earlier, that we examine the motion in a moving coordinate system x, y, z, which is fixed by the equilibrium configuration of the system.) Thus, $\mu h\dot{y}_1=I\dot{\theta}$ where h is the height of the pyramid. But $\mu h^2+I=A$, the moment of inertia of the molecule perpendicular to the symmetry axis. By substitution we obtain for the first two terms of the kinetic energy $\mu A\dot{y}_1^2/C$. It has appeared simplest to develop the kinetic energy as a function of y_1 and one might continue to treat the motion using this coordinate. Such a treatment would suffer a disadvantage, however, in that y_1 does not specify a geometric property of the system, since the actual geometric configuration is determined both by y_1 and by the tipping of the X_3 triangle. That is to say, it involves the momentum relation and hence implies that the positions of the particles are a function both of y_1 and of the masses. This difficulty, which becomes particularly important when we examine isotope effects, may be obviated by choosing a geometric coordinate, one which characterizes a geometric property of the system and is independent of the masses. For example we may use the perpendicular distance between the Y atom and the normal to the X_3 plane through G. Let this be called y. Clearly

$$y=y_1+h\theta \quad \text{or} \quad y=(1+2\mu h^2/C)y_1=(2A/C)y_1$$

by reason of the momentum relation.

Up to the present we have considered a displacement y perpendicular to the symmetry axis and lying in the plane of the paper (Fig. 1). Let the corresponding displacement perpendicular to the plane of the paper be x. Making the indicated substitutions we obtain

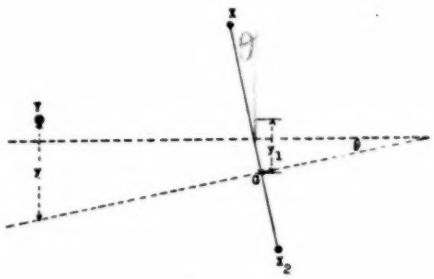

FIG. 1.

$$T=\tfrac{1}{2}(\mu C/2A)(\dot{x}^2+\dot{y}^2)+T_0.$$

The kinetic energy T_0 of the X atoms within their plane and relative to their center of gravity G has appeared many times in the literature[5] since it is the kinetic energy for a triatomic molecule. We begin by expressing it as a function of q_1, q_2, and q_3, the changes in distance between pairs of atoms.

$$T_0=\tfrac{1}{2}m\{(5/9)(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2) -(2/9)(\dot{q}_1\dot{q}_2+\dot{q}_1\dot{q}_3+\dot{q}_2\dot{q}_3)\}.$$

A linear transformation may now be made which diagonalizes T_0 and at the same time introduces symmetric coordinates. Let

$$\xi=(q_1-q_2)/3^{\frac{1}{2}}, \quad \eta=\tfrac{1}{3}(q_1+q_2-2q_3), \quad \zeta=\tfrac{1}{3}(q_1+q_2+q_3),$$

in which case $T_0=\frac{1}{2}m(\dot{\xi}^2+\dot{\eta}+\dot{\zeta}^2)$. The displacements corresponding to ξ, η, and ζ are shown in Fig. 2 and it is at once evident that ξ and η form a degenerate pair capable of describing a $\perp$ vibration. ζ belongs to the other symmetry class and hence for our present purpose it may be disregarded.

The motions corresponding to ξ and η are subject to the condition that the linear and angular momenta of the system must remain zero. This serves to determine both the direction and magnitude of the actual space displacements of the particles which may be characterized as fol-

[5] N. Bjerrum, Verh. d. D. Phys. Ges. **16**, 737 (1914).

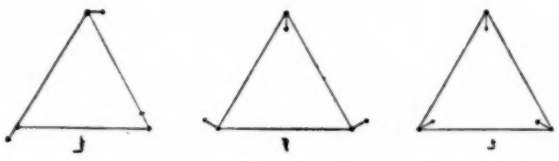

FIG. 2.

lows. (1) The displacement of any individual atom in the ξ motion is perpendicular to its displacement in the η motion. (2) The displacements of all the particles are the same and are given, respectively, by $d_i=\xi/3^{\frac{1}{2}}$ and $d_i=\eta/3^{\frac{1}{2}}$ where i is the number of the atom and runs from 1 to 3.

The total kinetic energy thus becomes

$$T=\tfrac{1}{2}m\{\alpha(\dot{x}^2+\dot{y}^2)+\dot{\xi}^2+\dot{\eta}^2\},$$

where $\alpha=\mu C/2mA$.

The potential energy may be written as a general quadratic form involving the arbitrary coefficients a, b, and c.

$$V=\tfrac{1}{2}\{a(x^2+y^2)+b(\xi^2+\eta^2)+2c(x\xi+y\eta)\}.$$

Although there are ten coefficients entering a general quadratic form containing four variables, the above expression is the most general one which may be used for the potential energy. This is due to the axial symmetry of the molecule, which insures first, that x and y and also ξ and η must enter on the same footing, and second, that the coefficients of such terms as xy, $x\eta$, etc., must vanish.

The Hamiltonian clearly may be divided into the sum of two identical Hamiltonians, the first a function of x and ξ and the second of y and η. Either of these may be treated by the method of normal vibrations, which yields the following relations between the λ's, where the normal frequency $\nu_i=\lambda_i^{\frac{1}{2}}/2\pi$:

$$m(\lambda_2+\lambda_4)=a/\alpha+b, \quad m^2\lambda_2\lambda_4=(ab-c^2)/\alpha.$$

This result is in agreement with the expressions obtained by J. E. Rosenthal[6] for the frequencies of the YX_3 molecule although the notation is somewhat different. We reproduce it here merely because it is one of the steps in the calculation of the internal angular momentum factors ζ_2 and ζ_4.

[6] J. E. Rosenthal, Phys. Rev. **47**, 235 (1935). The relations between our constants and those of Dr. Rosenthal are $A=a$, $3D=b$, and $3E^2=c^2$.

It is now necessary to transform to the normal coordinates x_2, x_4, y_2, and y_4 whereby

$$H=H_1(x_2, x_4)+H_1(y_2, y_4),$$

$$H_1(x_2, x_4)=\tfrac{1}{2}(p_{x_2}^2+p_{x_4}^2+\lambda_2x_2^2+\lambda_4x_4^2).$$

The normal coordinates x_2, x_4 are related to x and ξ by means of a linear transformation whose coefficients are proportional to the first minors of the determinant which gave the λ's. We find

$$x=\Sigma A_ix_i, \quad \xi=\Sigma B_ix_i, \quad i=2, 4,$$

where $A_i=(m\lambda_i-b)/[m\alpha(m\lambda_i-b)^2+mc^2]^{\frac{1}{2}}$,

$$B_i=c/[m\alpha(m\lambda_i-b)^2+mc^2]^{\frac{1}{2}}.$$

Identical expressions connect y_2 and y_4 with y and η.

The angular momentum of the entire system might be determined by finding the angular momentum of each particle and summing. However it will be more convenient to divide the molecule into two parts, the Y atom and the X_3 group. Now, as is well known, the angular momentum of any group of particles (say X_3) is equal to the angular momentum of the particles relative to their center of gravity G, plus the contribution due to the center of gravity. Thus Y and G together, which constitute a two particle group, will possess an angular momentum $\mu(x_1\dot{y}_1-y_1\dot{x}_1)=\mu(C/2A)^2(x\dot{y}-y\dot{x})$. The angular momentum of the X_3 group relative to G may be found by considering the momentum of any one particle and multiplying by 3. We obtain $-m(\xi\dot{\eta}-\eta\dot{\xi})$. This expression is preceded by a minus sign since it is oppositely directed from the momentum of Y and G. The reader may easily verify this statement by drawing several phases of the motion illustrated in Fig. 2. The momentum due to Y and G has the same direction as the rotation of the electric moment, since Y and G are the carriers of the electric charges.

We may now transform to the normal coordinates and $(x\dot{y}-y\dot{x})$ becomes $A_2^2(x_2\dot{y}_2-y_2\dot{x}_2)+A_4^2(x_4\dot{y}_4-y_4\dot{x}_4)+A_2A_4(x_2\dot{y}_4-y_4\dot{x}_2+x_4\dot{y}_2-y_2\dot{x}_4)$. The eigenvalues of these terms may be found very easily when we recall that the wave functions are the usual Hermitian orthogonal functions in the variables $2\pi(\nu_i/h)^{\frac{1}{2}}x_i$ and $2\pi(\nu_i/h)^{\frac{1}{2}}y_i$. We obtain $A_2^2h/2\pi$ or $A_4^2h/2\pi$ for the first excited states of ν_2 and ν_4, respectively. Thus the

contribution to ζ_i from the motion of Y and G is $\mu(C/2A)^2A_i^2$. From similar reasoning one obtains the remaining part of ζ_i. which is due to the momentum of the X_3 particles relative to G.

Adding these two terms and substituting for A_i and B_i we have finally

$$\zeta_i=(C/2A-\delta_i)/(1+\delta_i) \qquad i=2, 4,$$

where $$\delta_i=2mAc^2/\mu C(m\lambda_i-b)^2.$$

The sum $\zeta_2+\zeta_4$ may now be determined by direct substitution. The resulting complicated expression may be reduced by means of the relations between λ_2 and λ_4 to the simple form $\Sigma\zeta=C/2A-1$. The fact that $\Sigma\zeta$ turns out to be independent of the force constants a, b, and c, is both an example of the general theorem relating to $\Sigma\zeta$ and a verification that our calculations have been free from algebraic errors.

These formulae may be used in the analysis of the spectra of NH_3 and ND_3. The experimental data are as follows.

The long wave perpendicular band ν_4 of NH_3 has been mapped by E. F. Barker[7] and has its center at 1631 cm^{-1}. It shows an intense central region of absorption which is between 30 and 40 cm^{-1} wide. This no doubt corresponds to a clustering of zero branch lines whose spacing $\Delta\nu_4$ may be estimated at around 3 cm^{-1}. The spectrum of ND_3 has been studied by M. V. Migeotte and E. F. Barker[8] who have found both of the fundamental perpendicular bands, $\nu_2=2556$ and $\nu_4=1188$. The short wave bands consist of a set of equally spaced lines (the zero-branch lines) with a spacing $\Delta\nu_2\cong 5.2$ cm^{-1}. The long wave band ν_4 exhibits a strong central absorption corresponding to a spacing of from 1 to 2 cm^{-1}. We wish to express our gratitude to Professor Barker and Dr. Migeotte for allowing us to reproduce here a portion of their unpublished data.

We shall adopt the following procedure. By means of the observed band centers ν_4 of NH_3 and ν_2, ν_4 of ND_3, the potential constants a, b, and c may be determined. From a knowledge of these constants, the ζ's and finally the fine structure spacings may be computed and compared with the observed spacings. In making all these calculations we require the ratio of the moments of inertia $C/2A$. To find this we shall use the line spacings of the pure rotation spectra of the ammonias. Wright and Randall[9] obtained for NH_3 that $h/4\pi^2A=19.88$ whereas Barnes, Benedict and Lewis[10] found for ND_3 that $h/4\pi^2A=10.22$ cm^{-1}. These data yield $C/2A=0.825$ and 0.847 for NH_3 and ND_3, respectively. Unfortunately this ratio is extremely sensitive to small changes in the line spacings and appears to be determined with an accuracy of not better than 5 to 10 percent. The potential constants are then found to be $a=9.42$, $b=4.12$, $c=\pm 3.97\times 10^5$ dynes/cm. Here again the errors are considerable, amounting to at least 5 percent. This is due to two causes: first to the inaccuracy in $C/2A$; second, to the fact that we have used the observed positions of the fundamental bands rather than the normal frequencies which are demanded by the theory. The normal frequencies themselves may be found only when all the anharmonic constants are known.

TABLE I. *Values of the ζ's and line spacings.*

	ζ_2	$\Delta\nu_2$ COMP.	$\Delta\nu_2$ OBS.	ζ_4	$\Delta\nu_4$ COMP.	$\Delta\nu_4$ OBS.
NH_3	−0.004	7.15	—	−0.171	5.76	~3 to 4
ND_3	+ .104	4.81	5.2	− .257	2.66	~1 to 2

The results of the calculations on the ζ's and the line spacings are shown in Table I.

The agreement between the computed and observed $\Delta\nu$ is not at all satisfactory although it appears to be best in the one case, $\Delta\nu_2$ of ND_3, where the experimental data are most precise. We feel that these results do not constitute any real test of the theory. They show rather that the $\Delta\nu$ are sensitive to the potential constants and to the ratio $C/2A$, and consequently it may be possible through them to obtain more exact values for the molecular constants. This must wait however in the case of the ammonias until further measurements are available on the line spacings.

The next class of molecules to be considered is the axial system ZYX_3 to which the methyl halides belong. There exist three perpendicular bands which are determined by six potential constants. The task of computing the individual ζ's in terms of the six constants becomes rather

[7] To be published in the near future.
[8] M. V. Migeotte and E. F. Barker, Phys. Rev., in press.
[9] N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).
[10] R. B. Barnes, W. S. Benedict and C. M. Lewis, Phys. Rev. **45**, 347 (1934).

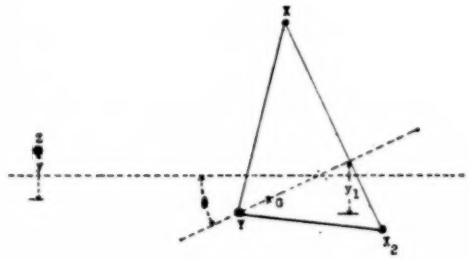

FIG. 3.

arduous and for the present we shall merely obtain an expression for $\Sigma\zeta$ over the three perpendicular fundamental bands. Now $\Sigma\zeta$ is independent of the potential constants and therefore may be calculated by using any limiting force field. The result is then correct for all force fields.

We have chosen the limiting field to be such that the YX_3 group is held together by very strong forces while the Z particle is very weakly bound to the YX_3 group. The three perpendicular frequencies may now be characterized by ν_2 and ν_4 which correspond to a motion within the YX_3 group itself, the Z atom standing still, and ν_6, which is to be correlated with a vibration of the Z atom against a rigid pyramid YX_3. In this latter mode of vibration, the Z atom moves in a path perpendicular to the symmetry line against the center of gravity G of the YX_3 pyramid. This motion is shown in Fig. 3. In order to preserve the constancy of the angular momentum the pyramid must tip through the angle θ.

In this extreme type of force field the frequencies ν_2 and ν_4 belong to a motion of the YX_3 group alone and hence we have $\zeta_2+\zeta_4=C/2A'-1$ where A' is the moment of inertia of the YX_3 pyramid about an axis perpendicular to the symmetry axis and drawn through G. C is the moment of inertia of the YX_3 group, or, in fact, of the entire molecule ZYX_3 along the symmetry axis. It remains now to compute ζ_6. The total kinetic energy for the motion ν_6 is the sum of the energies of Z, of G and of the tipping of the pyramid.

$$T=\tfrac{1}{2}(\mu_1\dot{y}^2+A'\dot{\theta}^2),$$

where y is the sum of the displacements of Z and of G and μ_1 is the reduced mass $\mu_1=M_1(M_2+3m)/M_1+M_2+3m$; M_1, M_2 and m are the masses of a Z, Y and X atom, respectively.

The coordinates y and θ are not independent but are connected by the momentum relation

$$u_1b\dot{y}=A'\dot{\theta}$$

where b is the equilibrium distance between Z and G. Thus

$$T=\tfrac{1}{2}(\mu_1+\mu_1^2b^2/A')\dot{y}^2.$$

This expression may be somewhat simplified by recalling that $A'+\mu_1b^2=A$, the moment of inertia of the whole molecule about an axis perpendicular to the symmetry axis. We shall also introduce the coordinate x, corresponding to a displacement of Z relative to G, out from the plane of the paper in Fig. 3.

$$T=\tfrac{1}{2}(\mu_1A/A')(\dot{x}^2+\dot{y}^2).$$

The kinetic energy may however be written as a function of the normal coordinates x_6 and y_6.

$$T=\tfrac{1}{2}(\dot{x}_6^2+\dot{y}_6^2)$$

and therefore we have the relations

$$x=(A'/\mu_1A)^{\frac{1}{2}}x_6 \quad \text{and} \quad y=(A'/\mu_1A)^{\frac{1}{2}}y_6.$$

The total angular momentum of the system about the symmetry axis is most easily obtained by decomposing it into two parts. First, consider the contribution due to the motion of Z and G. This is clearly $\mu_1(x\dot{y}-y\dot{x})$. The second contribution is that coming from the motion of the YX_3 pyramid relative to its center of gravity G. This becomes $\mu_2(x_1\dot{y}_1-y_1\dot{x}_1)$ where μ_2 is the reduced mass $3mM_2/(3m+M_2)$ and x_1, y_1 are the displacements of the Y atom relative to the center of gravity of the X_3 group, perpendicular to and in the plane of the paper (Fig. 3), respectively.[11] The coordinate $y_1=h\theta$ where, as earlier, h is the height of the YX_3 pyramid. Hence, through the momentum relation y_1 is connected with y. Thus $y_1=(\mu_1bh/A')y$ and the total angular momentum of the ZYX_3 molecule becomes

$$(\mu_1+\mu_2(\mu_1bh/A')^2)(x\dot{y}-y\dot{x})$$

or in terms of the normal coordinates

[11] In considering this second contribution we have treated the YX pyramid as two units, the Y atom and the X_3 group. It might be thought that there would be a third contribution to the angular momentum coming from the motion of the X_3 group relative to its center of gravity. This term is however zero since, relative to their center of gravity, the displacements of each X atom are always parallel to the symmetry axis.

$$[\mu_1+\mu_2(\mu_1 bh/A')^2](A'/\mu_1 A)(x_6\dot{y}_6-y_6\dot{x}_6).$$

The eigenvalues of $(x_6\dot{y}_6-y_6\dot{x}_6)$ may be found by the method indicated in the calculations on the YX_3 molecules. For the first excited state they are $\pm h/2\pi$. Therefore

$$\zeta_6=[\mu_1+\mu_2(\mu_1 bh/A')^2](A'/\mu_1 A).$$

A simple calculation reduces this to the form

$$\zeta_6=C/2A-C/2A'+1.$$

The sum over all the ζ's therefore becomes $\Sigma\zeta=C/2A$. We wish to emphasize again that, although this result has been obtained from a computation using a limiting and physically unreal force field, it will hold true for any actual force field. The conditions for its strict validity are, harmonicity of the motion and no resonance relations between the frequencies. It is clear that this method of the limiting fields may be used to determine the $\Sigma\zeta$ for any axial molecule.

The fundamental perpendicular bands of the methyl halide molecules have all been observed by Bennett and Meyer[12] and their fine structure measured. Since in the present theory $\Sigma\zeta$ and not the individual ζ's themselves have been computed, it will be possible to make use of the sum of the line spacings only. Adding the line spacings of the three perpendicular bands we obtain evidently[13]

$$\Sigma\Delta\nu=[(3-\Sigma\zeta)/C-3/A]h/4\pi^2$$
$$=(3/C-7/2A)h/4\pi^2.$$

The observations of Bennett and Meyer yield $\Sigma\Delta\nu=24.65$, 27.15, 28.32 and 28.5 cm^{-1} for CH_3F, CH_3Cl, CH_3Br and CH_3I, respectively. The moment of inertia A has been measured directly from the line spacing of the parallel type bands in the case of methyl fluoride[12] and methyl chloride[14] and found to be 39.5 and 50×10^{-40}. For the remaining methyl halides we have only the estimates[15] based upon the envelopes of the parallel bands, namely, 89 and 99×10^{-40}, respectively. These values are admittedly not very accurate, but small errors in them will have almost no influence upon the computation of C since the term $3/C$ is so much larger than $7/2A$.

The indicated substitutions are easily made and give the following numbers for the moment of inertia C of methyl fluoride to methyl iodide: 5.61, 5.35, 5.44, and 5.44×10^{-40}. The corresponding H−H distances are 1.84, 1.80, 1.81 and 1.81×10^{-8} cm. In the next section we shall find the moment of inertia of methane $A=5.47\times10^{-40}$ and $H-H=1.81\times10^{-8}$ through an analogous method. Direct measurements on the moment of inertia of methane through the line spacings of methyl deuteride[16] are now available and give $A=5.298$ and $H-H=1.785$. We feel that these results are to be interpreted by saying that, within the present limits of error, the dimensions of the H_3 triangle and presumably of the CH_3 group remain unchanged throughout the series of methane and the methyl halides. There are two principal sources of error: on the experimental side the line spacings of many of the methyl halide bands are not very accurately known; on the theoretical side we have taken no account of the departures from harmonic motion. The total error in C could be as high as 10 percent although probably it is nearer 5 percent. We do not mean to imply that the CH_3 group undergoes no change as we proceed from CH_4 to CH_3I, but only that our calculations show that whatever change does occur, must be smaller, possibly much smaller, than 5 to 10 percent.

§3. The Overtones of Axially Symmetric Molecules

Transitions from the normal state to excited states higher than the first result in overtone bands. The fine structure spacing of the perpendicular bands will evidently be given by the same formula as that for the fundamentals $\Delta\nu=[(1-\zeta)/C-1/A]h/4\pi^2$. It is our purpose to compute the ζ's appropriate for the lower overtones of the molecules YX_3 and ZYX_3. We shall begin by treating the overtones $2\nu_i$. As usual the

[12] W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

[13] In the preliminary note, Dennison and Johnston, Phys. Rev. **47**, 93 (1935), an error appeared in this formula which slightly affected the resulting values of the moments of inertia. Since the publication of the note, a more precise measurement has become available for the moment of inertia A of methyl chloride which is incorporated in the present paper.

[14] E. F. Barker and E. K. Plyler, J. Chem. Phys. **3**, 367 (1935).

[15] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43** 197 (1933).

[16] N. Ginsburg and E. F. Barker, J. Chem. Phys. **3**, 668 (1935).

wave function in first approximation is separable in the normal coordinates. Consider that part which depends upon x_i and y_i. It is now simpler to transform to polar coordinates ρ_i, θ_i where ρ_i is proportional to a displacement say of the Y atom perpendicular to the symmetry axis, and θ_i gives the angle of turning about the symmetry axis. Thus $\rho_i^2=x_i^2+y_i^2$ and $\tan\theta_i=y_i/x_i$. These coordinates and the resulting wave functions are identical with those employed in describing the CO_2 molecule.[17] The wave function of the normal state (at least that part depending upon ρ_i and θ_i) is $R_{(\rho)}{}^{00}$ while the excited state in question is characterized by the three functions $R_{(\rho)}{}^{22}e^{\pm 2i\theta}$ and $R_{(\rho)}{}^{20}$. The coefficients of $i\theta$ show that the eigenvalues of $(x_i\dot{y}_i-y_i\dot{x}_i)$ for the excited state are ± 2 and 0.

Now the electric moment perpendicular to the symmetry axis is proportional to x_i or to y_i, that is, to $\rho e^{\pm i\theta}$. It is thus clear that the matrix elements of the electric moment all vanish since the integrand is periodic in θ. This is to be expected, for up until now we have considered only the lowest order approximation, in which the motion is strictly harmonic and in which no overtone bands can appear. We must therefore consider the modifications to the wave functions caused by deviations from harmonicity. The perturbing function $\lambda V'$ may be expanded as a periodic series in 3θ, the factor 3 signifying the threefold symmetry of the X_3 group. Thus

$$\lambda V'=\lambda\sum_m F_{(\rho)}{}^m e^{3im\theta}.$$

For the present discussion where we are interested in the possibility but not the actual probability of a transition, it is sufficient to consider the effect of the perturbation on the wave function of the normal state. By the usual formulae of perturbation theory we obtain $R^{00}+\lambda\sum_{m=-\infty}^{\infty} S^m e^{i3m\theta}$ where S^m is a function of ρ. It is now evident that no transitions resulting in perpendicular bands occur to the state R^{20}. The matrix element of the electric moment does however receive a contribution from the two wave functions $S^1e^{+i3\theta}$ and $R^{22}e^{+i2\theta}$ and also from the terms $S^1e^{-i3\theta}$ and $R^{22}e^{-i2\theta}$. These considerations give us an answer to the question of the appropriate ζ. It must have the magnitude $2\zeta_i$ (from the magnitude of the eigenvalue of $(x_i\dot{y}_i-y_i\dot{x}_i)$ and it must have the negative sign. This last conclusion, namely, that the direction of rotation of the electric moment is reversed may be seen from the fact that in the fundamental bands we connect R^{00} and $R^{11}e^{i\theta}$, and the coefficient of $i\theta$ goes $0\rightarrow 1$. In the present case the coefficient of $i\theta$ goes $3\rightarrow 2$ thus giving a reversal of direction.

The next overtone $3\nu_i$ corresponds to a transition from the normal state to an excited state described by the four wave functions $R^{31}e^{\pm i\theta}$ and $R^{33}e^{\pm i3\theta}$. By an application of the reasoning just employed, it appears that a transition resulting in a perpendicular type band may occur only to $R^{31}e^{\pm i\theta}$. The ζ characterizing the fine structure spacing is therefore just ζ_i itself. In this manner we could compute the ζ for any harmonic $n\nu_i$ but the result would be rather meaningless for large values of n since here the influence of the anharmonic terms will become appreciable. The reader must not confuse the fact that although we have made use of the existence of the anharmonicity in order to find the selection rules, we have not taken account of its effect on the fine structure.

One further type of overtone may be discussed profitably, namely, the combination band $\nu_i+\nu_k$. Three possibilities exist. First ν_i and ν_k may both be parallel bands, in which case $\nu_i+\nu_k$ is also parallel and hence not included in the present treatment. Secondly, one of the bands, say ν_i, is perpendicular while the other ν_k is parallel. The presence of energy in a parallel mode of vibration does not at all change the internal angular momentum and hence the ζ for the overtone $\nu_i+\nu_k$ is just ζ_i. The third case where ν_i and ν_k are both perpendicular is somewhat more complex. The excited state is fourfold degenerate and is specified by the wave functions $R_i{}^{11}R_k{}^{11}e^{\pm i(\theta_i+\theta_k)}$ and $R_i{}^{11}R_k{}^{11}e^{\pm i(\theta_i-\theta_k)}$. The internal angular momentum is additive and depends upon the coefficients of θ_i and θ_k; hence the angular momentum belonging with these wave functions is $\pm(\zeta_i+\zeta_k)h/2\pi$ and $\pm(\zeta_i-\zeta_k)h/2\pi$, respectively. The electric moment with components μ_x and μ_y is given by $\mu_x+i\mu_y=a_i\rho_ie^{i\theta_i}+a_k\rho_ke^{i\theta_k}$ where a_i and a_k are proportionality factors. We must now consider the influence of the anharmonicity on the wave func-

[17] A. Adel and D. M. Dennison, Phys. Rev. **43**, 716 (1933).

tions. The perturbing energy $\lambda V'$ is composed of a sum of terms of the type

$$\lambda F(\rho_i\rho_k)e^{i[m_1\theta_i+(3m_2-m_1)\theta_k]}$$

where m_1 and m_2 are integers. The threefold symmetry of the molecule shows itself in the fact that the sum of the coefficients of θ_i and θ_k must be a multiple of three.

As before it will be sufficient to obtain the form of the perturbed wave function of the normal state. This is evidently

$$R_i^{00}R_k^{00}+\lambda \sum_{m_1,\ m_2} S^{m_1,\ m_2}e^{i[m_1\theta_i+(3m_2-m_1)\theta_k]}.$$

A simple trial now makes it clear that no transitions of the perpendicular type may occur from the normal state to the wave functions $R_iR_ke^{\pm i(\theta_i-\theta_k)}$ since the integral is always periodic either in θ_i or θ_k. Transitions may occur, however, to the states $R_iR_ke^{\pm i(\theta_i+\theta_k)}$. The particular terms of the perturbed normal state wave functions which furnish a nonperiodic integrand have the following dependence upon the angles, $e^{\pm i(\theta_i+2\theta_k)}$ or $e^{\pm i(2\theta_i+\theta_k)}$. From these considerations we see that the ζ appropriate for the band $\nu_i+\nu_k$ has the magnitude $\zeta_i+\zeta_k$ and that it has the negative sign. The reasoning which fixes the sign is identical with that employed in the case of the overtone $2\nu_i$.

An application of this result may be made to the band of NH_3 which lies at about 2μ. The band,[18] which is of the perpendicular variety, is composed of a set of equispaced lines with a spacing constant $\Delta\nu=9.98$ cm^{-1}. The position of the band center would be consistent with its identification as either $\nu_1+\nu_4$ or $\nu_2+\nu_4$ where ν_2 and ν_4 are the perpendicular fundamentals and ν_1 is the high frequency parallel band. In the first case $\nu_1+\nu_4$, the ζ would be equal to ζ_4 and the fine structure should resemble that of the fundamental ν_4. However, this is not what is observed since ν_4 shows a strong central region of absorption corresponding to $\Delta\nu\sim3$ or 4. Under the second identification, $\nu_2+\nu_4$, the appropriate ζ would be $-(\zeta_2+\zeta_4)=1-C/2A$. Substituting in the formula for the line spacing we obtain $\Delta\nu=-h/8\pi^2A$. That is to say, the spacing should be just half the spacing of a parallel type band or 9.94 cm^{-1}, in very good agreement with the observations.

[18] Stinchcomb and Barker, Phys. Rev. **33**, 305 (1929).

The only other existing data on the fine structure of overtones of axial molecules appear to be those by Nielsen and Barker[19] on methyl chloride. The methyl chloride molecule possesses three fundamental perpendicular bands ν_2, ν_4, and ν_6. The fine structure of each has been measured by Bennett and Meyer[12] and found to be 8.2, 12.0 and 6.95 cm^{-1}, respectively. From these values, together with the moments of inertia A and C already cited, we obtain $\zeta_2=0.100$, $\zeta_4=-0.268$ and $\zeta_6=0.220$.

Nielsen and Barker observed a perpendicular band at about 6100 cm^{-1} which they identify with $2\nu_2$. The appropriate ζ for this overtone we computed to be $-2\zeta_2=-0.200$, which yields $\Delta\nu=11.3$ cm^{-1}. The experimental value of the spacing was 12.0 cm^{-1}.

The next perpendicular bands which they resolved lie at about 4360 and 4460 cm^{-1} and were labeled $\nu_2+\nu_3$ and $\nu_2+2\nu_5$. These correspond to the sum of a perpendicular ν_2 with a parallel frequency ν_3 or $2\nu_5$ and accordingly should have the $\zeta=\zeta_2$ and $\Delta\nu=8.2$ cm^{-1}. Actually they were found to have the spacings 8.4 and 8.6 cm^{-1}, respectively.

The final perpendicular region observed by Nielsen and Barker lies at 2462 cm^{-1} and shows a spacing of 9.7 cm^{-1}. They identified this band as $\nu_6+2\nu_5$ in which case $\zeta=\zeta_6$ and $\Delta\nu=6.95$ cm^{-1} in bad agreement with the measurements. A second identification which would yield essentially the same position for the band center is $\nu_4+\nu_6$. The appropriate ζ for such a combination is $-(\zeta_4+\zeta_6)=+0.048$ giving $\Delta\nu=8.74$ cm^{-1}.

The agreements which have been obtained between the predicted and observed line spacings of the perpendicular overtone bands of ammonia and methyl chloride we regard as very satisfactory. The deviations which are in no case larger than 10 percent are no doubt caused by the effect of the anharmonic terms whose influence is of course greater on the overtone bands than on the fundamentals.

§4. Spherically Symmetric Molecules

The symmetrical molecule YX_4 possesses four fundamental frequencies ν_1, ν_2, ν_3, and ν_4 which are single, doubly, triply and triply degenerate,

[19] A. H. Nielsen and E. F. Barker, Phys. Rev. **46**, 970 (1934).

respectively. The first two, ν_1 and ν_2 involve no motion of the Y atom and are consequently inactive in the infrared. On the other hand ν_3 and ν_4 are both active and correspond in first approximation to isotropic harmonic oscillators in space. Each of these latter may possess an internal angular momentum $\zeta_i h/2\pi$ and we shall first sketch the method of calculating ζ_3 and ζ_4 as functions of the potential constants.

The tetrahedral system YX_4 has nine degrees of vibrational freedom and hence must be described by nine coordinates. It seems very convenient and straightforward to specify them in the following manner. The positions of the four X particles may be fixed relative to their center of gravity G by means of the mutual displacements $q_1, q_2, \cdots q_6$ of the particles along the edges of the tetrahedron defined by the equilibrium configuration X_4. Let q_1 and q_2, q_3 and q_4, q_5 and q_6 relate to opposite edges of the tetrahedron. Finally, the displacement of Y relative to G may be given by three Cartesian coordinates x, y, z. These rectangular axes may be chosen in any manner, but it is convenient to let x, y, and z be lines perpendicular to the opposite edges of the equilibrium tetrahedron X_4 1 and 2, 3 and 4, and 5 and 6, respectively. This numbering of the edges corresponds with the subscripts of the q's.

The potential energy of the system V can now be written as a general quadratic form in the nine coordinates. The number of independent constants is greatly reduced, however, by reason of the tetrahedral symmetry and has been shown to be only five.[20] The number and the nature of these constants may be explained by the following description. The axes x, y and z are all equivalent and hence x^2, y^2, and z^2 have the same coefficient, say a. Similarly all the q^2 have the same coefficient, b. There are two types of cross products between the q's, first, cross products between adjacent edges (for example q_1q_3) and second, cross products between opposite edges, as q_1q_2. These two classes require the constants c and d, respectively. Finally, the tetrahedral symmetry is unchanged by reversing the direction of one of the Cartesian axes, say the x axis, and simultaneously interchanging the two opposite edges in this case q_1 and q_2. Thus there may be a cross product term of the sort $x(q_1-q_2)$ but no terms such as xy. Hence

$$\begin{aligned}V=\tfrac{1}{2}\{&a(x^2+y^2+z^2)+b(q_1^2+q_2^2+q_3^2+q_4^2+q_5^2+q_6^2)\\&+2c(q_1q_3+q_1q_4+q_1q_5+q_1q_6+q_2q_3+q_2q_4\\&+q_2q_5+q_2q_6+q_3q_5+q_3q_6+q_4q_5+q_4q_6)\\&+2d(q_1q_2+q_3q_4+q_5q_6)+2e[x(q_1-q_2)\\&+y(q_3-q_4)+z(q_5-q_6)]\}.\end{aligned}$$

The kinetic energy of the YX_4 molecule was found by Dennison[21] using coordinates identical with those defined here, except for a nonessential charge in the orientation of the xyz axes.

$$\begin{aligned}T=\tfrac{1}{2}\{&\mu(\dot{x}^2+\dot{y}^2+\dot{z}^2)+(5m/8)(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2\\&+\dot{q}_4^2+\dot{q}_5^2+\dot{q}_6^2)-2(m/8)(\dot{q}_1\dot{q}_3+\dot{q}_1\dot{q}_4+\dot{q}_1\dot{q}_5\\&+\dot{q}_1\dot{q}_6+\dot{q}_2\dot{q}_3+\dot{q}_2\dot{q}_4+\dot{q}_2\dot{q}_5+\dot{q}_2\dot{q}_6+\dot{q}_3\dot{q}_5+\dot{q}_3\dot{q}_6\\&+\dot{q}_4\dot{q}_5+\dot{q}_4\dot{q}_6)+2(m/8)(\dot{q}_1\dot{q}_2+\dot{q}_3\dot{q}_4+\dot{q}_5\dot{q}_6)\},\end{aligned}$$

where $\mu=4mM/(4m+M)$ and m and M are the masses of the X and Y particles, respectively. The determinant giving the normal frequencies $\nu_i=\lambda_i^{\frac{1}{2}}/2\pi$ may be readily solved and yields,

$$\begin{aligned}&m\lambda_1=4b+4d+16c, \quad m\lambda_2=b+d-2c,\\&m(\lambda_3+\lambda_4)=ma/\mu+2b-2d,\\&m^2(\lambda_3\lambda_4)=2m(ab-ad-2e^2)/\mu.\end{aligned}$$

The normal frequencies of the YX_4 molecule have already been computed by J. E. Rosenthal[20] as a function of five constants, A, B, C, D and E which are connected with our constants by the linear relations, $A=a$, $B=(b-d)/4$, $C=(b+d)/4-c/2$ and $D^2=e^2/2$. $E=(b+d)/4+c$.

The internal angular momentum associated with the frequencies ν_3 and ν_4 may be calculated by a method essentially similar to that employed in the treatment of the YX_3 molecule. The first minors of the normal determinant will give the coordinates x, y, z, $q_1 \cdots q_6$ as linear functions of the normal coordinates. These functions in the case of the motions ν_3 and ν_4 are indeterminate to the extent of the threefold degeneracy. This degeneracy may be removed if we assume that the angular momentum lies along some definite axis,

[20] J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).

[21] D. M. Dennison, Astrophys. J. **62**, 84 (1925).

say the z axis. This means that the amplitude of z is zero while the amplitude of x and y are equal but ninety degrees out of phase. The amplitudes of all the q's, and hence the actual space displacements of all particles, are then completely defined. The angular momentum may be divided into the two parts: that caused by the motion of the Y particle and G, namely, $\mu(x\dot{y}-y\dot{x})$ and that caused by the motion of the X particles relative to G. These two contributions are then added and evaluated in terms of the normal coordinates exactly as was done in the case of the YX_3 molecule. The calculation is somewhat complicated but eventually leads to the simple result[22]

$$\zeta_i=(\delta_i-\tfrac{1}{2})/(\delta_i+1),$$

where $\delta_i=4\mu e^2/m(\mu\lambda_i-a)^2$; $i=3, 4$.

The frequencies ν_3 and ν_4 belong to the same symmetry class and are the only fundamental frequencies of this class. Hence according to Teller's theorem $\zeta_3+\zeta_4$ should be independent of the force constants. Upon making the addition and using the relations between λ_3 and λ_4 we find $\zeta_3+\zeta_4=\frac{1}{2}$. This result may also be obtained from the formula $\Sigma\zeta=C/2A$ for the ZYX_3 molecule. In this latter system as the Z atom is changed into an X atom and the molecule assumes the tetrahedral form, the frequencies ν_2, ν_4 and ν_6, go over into the frequencies ν_3, ν_2 and ν_3 of YX_4, respectively.[23] Therefore the $\zeta_2+\zeta_4+\zeta_6=C/2A$ of ZYX_3 becomes $\zeta_3+\zeta_2+\zeta_4=C/2A=\frac{1}{2}$ for YX_4. We must now consider the following question. What is the internal angular momentum to be associated with the inactive frequency ν_2 of YX_4? By drawing the displacements of the particles it is easy to show that each X particle does indeed possess an angular momentum, but that these angular momenta are all equal and all directed either towards, or directly away from the central Y atom. Consequently the total angular momentum vanishes and hence $\zeta_2=0$. Thus $\zeta_3+\zeta_4=\frac{1}{2}$ in agreement with the result obtained by direct calculation.

The formulae for the ζ's are of great practical importance in the interpretation of the spectrum of methane. In the first place, they enable one to calculate the moment of inertia by summing the line spacings of the bands ν_3 and ν_4. Thus $\Delta\nu_3+\Delta\nu_4=(2-\zeta_3-\zeta_4)h/4\pi^2A=3h/8\pi^2A$. Secondly, they supply a fifth datum which together with the values of the four fundamental frequencies just allows us to determine the five potential constants of the molecule. The measurements of Cooley[24] gave the following values for the line spacings. $\Delta\nu_3=9.771$ cm^{-1} and $\Delta\nu_4=5.409$ cm^{-1}. Following through the indicated substitutions we find $A=5.47\times10^{-40}$, $\zeta_3=0.0345$, $\zeta_4=0.4655$. The molecular dimensions are $H-H=1.81\times10^{-8}$ and $C-H=1.11\times10^{-8}$ cm.

The values of the fundamental frequencies $\nu_1=2914$, $\nu_2=1520$, $\nu_3=3014$, and $\zeta_4=1304$ cm^{-1} together with either ζ_3 or ζ_4 (the ζ's are not independent since $\Sigma\zeta=\frac{1}{2}$) serve to fix the potential constants. We find

$a=7.670\times10^5$ dynes/cm $\quad c=-0.018 \quad e=\pm1.807$
$b=1.616 \quad\quad\quad\quad\quad d=-0.289$

or in Dr. Rosenthal's notation

$A=7.670\times10^5$ dynes/cm $\quad C=0.341 \quad\quad E=0.313$
$B=0.476 \quad\quad\quad\quad\quad D=\pm1.278.$

These data do not determine the sign of e or of D, but the recent paper of Ginsburg and Barker[16] on the spectrum of methyl deuteride shows conclusively that the positive sign is the one to be chosen. The work just cited is extremely important from our point of view since the values of the fundamental frequencies of CH_3D together with the line spacing of the parallel bands yield independent values for the moment of inertia and the potential constants of methane. It turns out that $A=5.298\times10^{-40}$, which is about 3 percent lower than our figure. This agreement is quite as good as could be expected from a theory which neglects second-order perturbations. The potential constants obtained by Ginsburg and Barker differ from ours by amounts around 5 percent. We regard a divergence of this order of magnitude as being inevitable for the following reason. Ginsburg and Barker in their calculations were forced to use the observed positions of the fundamental bands and not the actual normal frequencies themselves. The difference between these two is of the order of 10 to 50 cm^{-1} and will introduce

[22] The formula for ζ_i appears to be slightly different from that published by us earlier. The difference is due solely to a small change in the notation and to the fact that we there employed Dr. Rosenthal's constants.

[23] D. M. Dennison, Rev. Mod. Phys. **3**, 304 (1931).

[24] J. P. Cooley, Astrophys. J. **62**, 73 (1925).

errors into the potential constants of around 5 percent. Thus we do not believe that the constants derived from the spectrum of methyl deuteride are essentially more accurate than those quoted here. A second way to make this clear is to calculate the frequencies of CH_3D by using our potential constants and the formulae of Dr. Rosenthal.[25] The differences between the calculated and observed frequencies are 18, 39, 22, 17, 7 and 5 cm^{-1}. But these are just of the order of magnitude of the shift in the position of a band caused by the existence of anharmonic terms in the potential.

The spectrum of methyl deuteride presents one further point where we may apply our theory and that is the fine structure spacing of the perpendicular bands ν_2, ν_4 and ν_6. In the formula $\Delta\nu_i=[(1-\zeta_i)/C-1/A]h/4\pi^2$ the moments of inertia A and C are known. The internal angular momentum factors ζ_i are completely fixed by the potential constants of methane and the masses of the particles. The actual computation of the ζ's was carried out by means of the method used previously, but eventually became so involved that recourse was had to a numerical evaluation. The only check that we have on the calculation is that the sum of the ζ's turns out to have its expected value $C/2A=0.370$. We obtained, $\zeta_2=0.03$, $\zeta_4=-0.25$, and $\zeta_6=0.59$ from which the line spacings $\Delta\nu_2=2.3$ $\Delta\nu_4=5.2$ and $\Delta\nu_6=-3.3$ cm^{-1} are readily deduced.

The observations of Ginsburg and Barker are as follows. The frequency ν_2 lies at 2983.0 cm^{-1} and has a strong central region of absorption indicating $\Delta\nu_2\sim 1$ cm^{-1}. This band, however, is in strong resonance interaction with the band $2\nu_4$ and consequently its line spacing will be greatly perturbed and no agreement with the theoretical spacing is to be expected.

The band ν_4 occurs at 1477.1 cm^{-1}. Its line spacing is somewhat irregular but appears to lie between 5 and 6 cm^{-1}, in good agreement with our estimate of 5.2 cm^{-1}. The frequency ν_6 at 1156.3 cm^{-1} consists of regularly spaced lines whose constant ranges from 3.8 to 4.5 cm^{-1}. Our value of 3.3 does not seem to be seriously in error.

[25] In the letter by Dennison and Johnston the frequencies of all the heavy methanes are computed and presented in a table which we omit in the present paper.

§5. The Overtones of Spherically Symmetric Molecules

A treatment of the overtones of the YX_4 molecule may be made along the same lines as that used in the discussion of the overtones of ZYX_3, but it is somewhat more complicated in that we are here concerned with tetrahedral rather than threefold symmetry. We shall consider only two types of overtone, $2\nu_i$, $i=3$, 4, and $\nu_3+\nu_4$.

Dennison and Ingram[26] in their paper on the overtones $n\nu_i$ of methane, calculated the multiplicity of the excited states. They showed that since the motion is similar to that of a three-dimensional isotropic oscillator, the wave functions may be expanded in terms of functions $\psi_{(x)}{}^{n_1}\psi_{(y)}{}^{n_2}\psi_{(z)}{}^{n_3}$ where $n_1+n_2+n_3=n$ the quantum number of the state. ψ is one of the Hermitian orthogonal functions and the rectangular coordinates x, y, z are proportional to the normal coordinates. (Because of the degeneracy the motions corresponding to ν_3 and ν_4 each require three normal coordinates.) The function $\psi_{(x)}{}^{n_1}\psi_{(y)}{}^{n_2}\psi_{(z)}{}^{n_3}$ is conveniently abbreviated by the symbol $(n_1n_2n_3)$ and it was shown that a perturbing function having tetrahedral symmetry will connect $(n_1n_2n_3)$ with $(n_1'n_2'n_3')$ providing n_1+n_1', n_2+n_2' and n_3+n_3' are either all even or all odd integers. One further statement must be made before beginning the analysis. A transition which is active must connect two wave functions for which one of the quantum numbers changes by one unit while the other two remain unchanged. Thus $(n_1n_2n_3)\rightarrow(n_1-1,\ n_2,\ n_3)$ corresponds to a nonvanishing electric moment in the x direction.

The normal state is characterized in first approximation by (000) but the perturbation will add terms of the sort $\lambda(n_1n_2n_3)$ where n_1, n_2, and n_3 are either all even or all odd integers. The first excited state is given (in first approximation) by the three functions (100), (010) and (001). Clearly, transitions to it from the normal state may occur resulting in the fundamental band ν_i. The internal angular momentum of this excited state is $\zeta_ih/2\pi$ and it is easy to show that its component, say along the z axis, is $(x\dot{y}-y\dot{x})\zeta_ih/2\pi$

[26] D. M. Dennison and S. B. Ingram, Phys. Rev. **36**, 1451 (1930).

Thus the eigenvalues of $(x\dot{y}-y\dot{x})$ for this state are $+1, 0, -1$.

Dennison and Ingram obtained the result that the second excited state $n=2$ is broken up into three states. The first and second of these are single and doubly degenerate, respectively, and both are described by linear combinations of the wave functions (200), (020) and (002). No transitions may occur to either of these states since it is impossible to select a wave function $(n_1n_2n_3)$ entering the perturbed part of the normal state wave function which will combine actively with the functions (200), (020) or (002). The third part of the state $n=2$ is triply degenerate and uses the functions (011), (101) and (110). A transition may occur from the normal state to this state by means of the particular term $\lambda(111)$ in the normal state wave function. Since the quantum number decreases rather than increases in going from the normal to the excited states, we would expect the ζ of $2\nu_i$ to be negative. This may be verified by direct calculation. The magnitude of the ζ depends upon the eigenvalues of $(x\dot{y}-y\dot{x})$ for the states (011), (101), and (110). A simple computation shows these to be $+1$, 0, and -1. Thus we obtain the result that the fine structure of the overtone $2\nu_i$, $i=3, 4$ has a spacing constant $(1-\zeta)h/4\pi^2A$ where $\zeta=-\zeta_i$.

The excited state leading to the overtone $n\nu_3+m\nu_4$ may be characterized by the symbol $(n_1n_2n_3)[m_1m_2m_3]$ where $n_1+n_2+n_3=n$ and $m_1+m_3+m_3=m$. The subscripts 1, 2, 3 refer to the xyz directions, respectively. The excited state of $\nu_3+\nu_4$ is ninefold degenerate; the wave functions consisting of functions of the type (100)[100], (010)[001], etc. The first problem is to find how the tetrahedral symmetry will regroup the nine functions. This is easily done by writing out the secular determinant, using any perturbing function $\lambda V'$ of tetrahedral symmetry. It soon appears that the only nonvanishing elements are those for which the changes in n_1+m_1, n_2+m_2 and n_3+m_3 are either all even or all odd integers. The secular determinant now shows that the nine degenerate levels arrange themselves into two triple states, one double, and one single state. Tetrahedral symmetry will not further reduce the degeneracy.

The first triple state is described by the wave functions

$$1/2^{\frac{1}{2}}\{(100)[001]+(001)[100]\},$$
$$1/2^{\frac{1}{2}}\{(010)[001]+(001)[010]\}$$

and

$$1/2^{\frac{1}{2}}\{(100)[010]+(010)[100]\}.$$

The second triple state is given by three functions of the type $1/2^{\frac{1}{2}}\{(100)[001]-(001)[100]\}$ while the double and single states are given by certain linear combinations of the functions (100)[100], (010)[010] and (001)[001]. To find the selection rules we must consider the perturbed part of normal state wave functions, the most significant terms of which for our purpose are of the type

$$\lambda\{(100)[011]+(010)[101]+(001)[110]\}.$$

These show that transitions may take place to the first triple state but not to the second triple state nor to the double or single state. Moreover in the term giving rise to the allowed transition, the quantum number decreases rather than increases, showing that the ζ will have the negative sign.

To obtain the magnitude of the ζ it is only necessary to calculate the eigenvalues of the angular momentum along some particular axis, say the z axis. The displacements used in computing the momentum are linear combinations of the normal coordinates with proportionality factors depending upon ζ_3 and ζ_4. Thus the angular momentum of the system about the z axis in units of $h/2\pi$ is,

$$(\zeta_3^{\frac{1}{2}}x_3+\zeta_4^{\frac{1}{2}}x_4)(\zeta_3^{\frac{1}{2}}\dot{y}_3+\zeta_4^{\frac{1}{2}}\dot{y}_4)$$
$$-(\zeta_3^{\frac{1}{2}}y_3+\zeta_4^{\frac{1}{2}}y_4)(\zeta_3^{\frac{1}{2}}\dot{x}_3+\zeta_4^{\frac{1}{2}}\dot{x}_4).$$

The eigenvalues of this function for the triple state in question are easily found to be $\pm\frac{1}{2}(\zeta_3+\zeta_4)$ and 0. Thus the ζ appropriate for the band $\nu_3+\nu_4$ is $-\frac{1}{2}(\zeta_3+\zeta_4)=-\frac{1}{4}$ and the line spacing of this overtone should be $5h/16\pi^2A$.

These results may now be compared with the experimental data. Although Cooley observed the positions of a number of the overtone bands of methane, he succeeded in resolving the fine structure of only one. He found a faint series of lines in the neighborhood of 3.5μ with a line spacing of about 15.3 cm^{-1}. This series he assumed to be the negative branch of a band with its center at 2824 cm^{-1} and hence he identified it as $\nu_2+\nu_4$.

Now the state ν_2 has no angular momentum and therefore $\nu_2+\nu_4$ should have the same line spacing as ν_4, that is, 5.4 cm^{-1}, in direct disagreement with the observations. A plausible way out of this difficulty is to assume that the faint series of lines found by Cooley is really the positive branch of the overtone $2\nu_4$ with its center lying at about 2608 cm^{-1}. Such an assumption is quite consistent with the observed data as far as it is now known. In that case the line spacing should be $(1+\zeta_4)h/4\pi^2A=14.8$ cm^{-1}, which is in very good agreement with the experimental determination.

The overtone bands of methane have also been studied by Moorhead.[27] He was able to resolve the fine structure of two bands; a band at 1.66μ which gave $\Delta\nu=10.4$ cm^{-1} and a band at 2.20μ with a spacing of 10.7 cm^{-1}. The first of these Moorhead identified as $2\nu_3$, which according to our theory should have a spacing of $(1+\zeta_3)h/4\pi^2A=10.5$ cm^{-1}. The band at 2.20μ which was also located by Cooley is probably $\nu_2+\nu_3$. Its line spacing should be the same as that of the fundamental ν_3 itself or about 9.8 cm^{-1}. This agreement, while less good, is still satisfactory.

In a recent paper Steward and Nielsen[28] report on the infrared absorption spectrum of silane, SiH_4. The general features of the spectrum are very similar to those of methane with the exception of the fact that the fine structure lines are not single but show satellites. This is probably due to the influence of the higher order perturbing terms which have not been included in the present theory. Ignoring as far as possible the multiplet structure, they obtain for the line spacing of the fundamentals ν_3 and ν_4 the values 5.7 and 3.5 cm^{-1}, respectively. From these data it follows that $\zeta_3=0.07$ and $\zeta_4=0.43$. Steward and Nielsen also observed the positions of a number of the overtones of silane and succeeded in partially resolving the fine structure of two of them, namely, the bands at 3095 cm^{-1} and 3153 cm^{-1}. These showed spacings of about 9.7 and 4.7 cm^{-1}, respectively. The band at 3095 cm^{-1} they identified as $\nu_3+\nu_4$. According to our theory it should have a spacing of $5h/16\pi^2A=7.7$ cm^{-1}. The second band they consider to be $\nu_1+\nu_4$, in which case it would have the same spacing as ν_4, that is, 3.5 cm^{-1}. The agreements in neither case are very satisfactory and certainly not as good as those found for methane. This is perhaps just what is to be expected since, if the higher order terms are sufficiently large to produce a splitting of the fine structure lines, they will no doubt appreciably affect the values of the line spacing.

Note added in proof: Very recently A. H. Nielsen and H. H. Nielsen have succeeded in resolving the two overtone bands of methane $\nu_1+\nu_4$ and $\nu_3+\nu_4$ (Phys. Rev., this issue). They obtain the spacing constants 5.3 and 13.5 cm^{-1}, respectively. According to our theory the spacing of $\nu_1+\nu_4$ should be just that of ν_4, namely, 5.4 cm^{-1} while the spacing of $\nu_3+\nu_4$ is $5h/16\pi^2A=12.6$ cm^{-1}. We wish to express our appreciation to the authors of this paper for allowing us to see and use their unpublished data.

[27] G. J. Moorhead, Phys. Rev. **39**, 83 (1932).
[28] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 828 (1935).

DECEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

Geiger-Counter Characteristics with Applied Potentials Reversed

D. B. Cowie, *Bartol Research Foundation of the Franklin Institute*

(Received September 16, 1935)

The paper describes experiments made with Geiger-Müller counters in which the cylinder potential is positive with respect to the wire instead of negative as ordinarily used. The counter operates under reduced efficiency with this reversed condition. When used as a double coincidence set the reduction in efficiency is greater than for a single counter. The paper also describes experiments confirming a view that the inefficiency of the reversed counter may be explained by supposing the counter action to be produced when a positive ion strikes the wire and liberates from it a secondary electron. Whenever such an electron is liberated a discharge takes place, but the probability of liberation is low. However, it seems reasonable that the probabilities of such liberation of secondary electrons as found by Penning and others stands in agreement with the efficiency observed in the counter experiments cited above.

THE Geiger-Müller counter connected normally with the wire at a positive potential with respect to the cylinder, has been used as a means of detecting various ionizing rays. It is well known that the counting action takes place with the potentials reversed, but it has been noticed that the rate of a reversed counter is much lower than with the potentials connected in the normal direction. For example, a double-coincidence[1] circuit, in which the record was made when the two counters discharged simultaneously, recorded two rays per minute with the potentials in the normal direction, while very few were recorded in a period of twelve hours with the potentials reversed. At first sight there is nothing remarkable in this result since one may contend that the counters operate by the release of an electron from the gas by an ionizing ray, with the subsequent transportation of the electron to the central wire, where under the large fields existing there it precipitates ionization by collision. With the potentials reversed, the released electron is carried away from the wire and the conditions for ionization do not develop. However, such a view discards the possibility that a positive ion when carried to the wire under a high potential difference may precipitate a discharge by secondary actions involving the emission of electrons from the wire. Such possibilities have in fact been studied by W. E. Danforth and others.

Possible Interpretation of the Results

Two main possibilities suggest themselves as an interpretation of the foregoing facts. The first instance, the failure of the counters to operate when used as a double-coincidence set, is to be sought in some cause which results in a time delay between the instant of breakdown of the two counters, this time delay being greater than the recovery time of the circuit used for recording. Under such conditions the recording circuit would fail to record rays even though they had passed through both counter tubes. Single counter discharges would, however, be recorded by a circuit designed to record singles. The time delay would presumably arise from the fact that the relatively low mobility of the positive ions would insure that the liberation of such ions from the gas by the cosmic ray at different distances from the wire, would result in an appreciable difference between the instant of arrival at the corresponding wires.

A possible alternative interpretation would be that the counters are inefficient with the potentials reversed and do not respond to all radiation passing through them.

In order to test this matter, two counters were arranged with independent counting circuits, so that the recovery time of the circuits was not involved, and coincidences were judged by the simultaneity of photographs of individual counts taken upon the same recording film. Two runs were made. In each the counters were 3.8 centimeters apart, from center to center. In the first run, the applied potential of the counter reversed was just below the 'plateau" of the potential-*vs.*-counting-rate curve of the normal counter. In the second run, it was well along the "plateau." The first experiment from a single counter gave 255 counts in an eight-hour run with the potentials reversed. The corresponding number of counts with the potentials in the normal direction was 2880. The value of the relative efficiency ϵ, of the reversed counter with respect to the normal counter is $255/2880 = 0.088$. Hence ϵ^2, the relative efficiency for double coincidences is 7.7×10^{-3}. The number of coincidences observed during the eight-hour run was 10, with the potentials reversed. The number of coincidences with the potentials applied in the normal direction was 960. This ratio, 10^{-4} to unity, agrees with the value 7.7×10^{-3} for ϵ^2 well within the statistical limits of accuracy determined by the 10 counts cited above.

In the second run the counting rates were different, as they should be, but the story of their ratios is as follows: With the potentials reversed, a run of 200 minutes gave 365 counts from a single counter. The corresponding number of counts for the same period with the potentials normal was 1600. The value of ϵ for this case was therefore $365/1600 = 0.23$. The value of ϵ^2 is therefore 0.053. The number of reversed coincidences for this period was 21, while the normal number with potentials applied normally

[1] The particular circuit used was that designed by G. L. Locher. The counters were argon filled, with their cylinders coated with copper oxide.

was 400. The ratio is 0.052, which again agrees with the value of ϵ^2.

In the foregoing experiments, the simple counter records gamma-rays as well as cosmic-ray particles, and to no negligible extent, while the coincidences between counters are concerned only with cosmic-ray particles. It is important to observe, however, that the foregoing conclusions are not vitiated by participation of the gamma-rays. For while the two sets of data from the single counter are influenced by gamma-rays as well as by cosmic-ray particles, they give the true value of ϵ, while the two experiments concerned with coincidences, though influenced only by cosmic-ray particles, give the true value of ϵ^2. All that is assumed is that the counter possesses 100 percent efficiency for potential applied normally, and an electron such as would be emitted by a gamma-ray from the counter wall has the same characteristics for its subsequent activities as has that charged particle which is the representative of the cosmic ray.

It is interesting to speculate as to the cause of the relative inefficiency of the reversed counter. Two possibilities suggest themselves. The first invoking only the electrons as the liberated entities responsible for the counter discharge. Since the electrons move away from the wire under the influence of the field, only those which are liberated very near the wire where the electric field is high can cause a discharge. In the case of a single counter the effect is therefore to limit the effective areas of the counter to a small region around the central wire, and so reduce the number of counts recorded. The double-coincidence counts, depending as they do upon the square of the area, will be much more affected by reversal than will the single counter; but even the single counter will be affected in proportion to the reduction of the effective area on reversal. As a matter of fact, the factor by which the single counting rate is reduced by reversal should be equal to the ratio of the effective counting area to the total counter area. We have called this factor ϵ and should expect that the coincidence counting rate would be reduced in the ratio of ϵ^2 to unity.

Considering the experimental values of ϵ, the limiting fields where an electron would just be able to produce a discharge would occur at the distance of 0.044 centimeter from the central wire for the lower voltage and in the case of the higher voltage at 0.12 centimeter from the central wire. The respective fields at these points are 4905 and 2398 volts per centimeter. Since it would be expected on this hypothesis that the fields at the edge of the sensitive volume should be identical, the discrepancy of the above values militates against the adoption of this hypothesis. The discrepancy is particularly striking if one compares these fields with the fields required for counter operation in the normal manner. At the threshold voltage the field at the surface of the wire is 54,000 volts per centimeter.

Following suggestions by T. H. Johnson and W. E. Danforth, a more probable interpretation of the inefficiency of the reversed counter can be made by supposing the counter action to be produced when a positive ion strikes the wire and liberates from it a secondary electron. Whenever an electron is so liberated a discharge results, but the probability of liberation is low. Penning[2] and others have investigated the probability of emission of secondary electrons from tungsten by impact of positive ions of several gases. The number of electrons per ion varies from 0.03 to 0.05 for energies of incident ions below 50 volts and increases nearly linearly with energy up to 0.42 for 1000-volt ions.

With the variations of the phenomenon attributable to adsorb gaseous layers, it seems probable that this range of probabilities stands in agreement with the efficiency found in the above counter experiments.

The writer wishes to express his appreciation of the help given by Professor W. F. G. Swann in formulating the final method of attack adopted in the problem.

[2] Penning, K. Akad. Wet. Amst. Proc. **33**, 841 (1930).

High Current Ion Sources for Nuclear Investigations

E. S. LAMAR, E. W. SAMSON AND K. T. COMPTON, *George Eastman Research Laboratory of Physics, Massachusetts Institute of Technology*

(Received October 8, 1935)

Since the capillary ion source described by Tuve, Dahl and Van Atta was a decided advance over previous types, it seemed desirable to investigate its possibilities further. The essential modification in the present design lies in the elimination of the auxiliary electrode for drawing ions out of the arc. This simplifies construction and greatly reduces the difficulties usually experienced in focusing ion beams. Currents as high as 4.2 milliamperes have been converged into a beam 12 mm wide with a focusing voltage of 10 kv. Possible explanations are presented for the observed dependence of the total ion current on arc current density, condition of the walls, and design of the outlet. Relative ease of starting and stability of the arc are discussed for various designs of tubes. When the arc was operated in hydrogen, the mass spectrograph showed a preponderance of diatomic and triatomic ions with proton fractions ranging from 5 to 20 percent of the total ion current. Ions other than those of hydrogen were not present in fractions exceeding 1 percent of the total. Evidence is presented for the breaking up of the heavy ions into protons and neutral particles on collision at high speed with gas molecules. Upper and lower limits are given for the efficiencies of these processes.

INTRODUCTION

RECENT developments in nuclear physics have served to emphasize the demand for high current sources of protons, deuterons, and helium ions. Further tests on the type of pure proton source described by Lamar and Luhr[1] have confirmed the conclusion reached by them that extreme cleanness of the various metal parts is necessary for the production of pure proton beams in this type of source. In their results there remained also much to be desired in the direction of increased ion current for a given gas transport. The capillary type ion source described by Tuve and his collaborators[2] gave ion currents, for a given gas transport, far in excess of those reported for the type of source mentioned above, though the proton purity was less. The present investigation was undertaken, therefore, in an effort to evaluate the various factors involved in the operation of the capillary discharge and to see in what directions one might hope for improvements. This paper is a presentation of the results of experiments carried on in this laboratory during the past year and reported first at the Washington meeting of the Physical Society. It is believed that our work, together with that of Dr. Tuve and his collaborators, constitutes a reasonably complete picture of the capillary type ion source.

[1] Lamar and Luhr, Phys. Rev. **44**, 947 (1933); Phys. Rev. **46**, 87 (1934).

[2] Tuve, Dahl and Van Atta, Phys. Rev. **48**, 315 (1935); Tuve, Dahl and Hafstad, Phys. Rev. **48**, 241 (1935).

APPARATUS AND EXPERIMENTAL PROCEDURE

A number of discharge tubes were tested, differing in detail one from another, but each having the same essential elements. A typical one is shown in Fig. 1. The metal envelope which enclosed the discharge was made in three pieces; a central stainless steel block, and two stainless steel tubes press fitted and soft soldered into the block. The discharge space consisted of two cylindrical enclosures (in every case 3.18 centimeters inside diameter) connected by a smaller hole or capillary. There was, in the side of the capillary, a tapered outlet through which ions, electrons, and neutral gas molecules might escape from the discharge. One of the enclosures contained an anode and the other an oxide-coated filament cathode. The stems for cathode and anode were supported by ground glass to metal joints on the ends of the steel tubes. These joints were made vacuum tight by means of picein w applied externally. The connection between the outlet side of the discharge tube and the miniature high voltage tube shown in the figure was also accomplished by means of picein wax. Hydrogen was introduced into the discharge tube and was pumped out of the high voltage tube with a pumping system having a net speed for air of 14 liters per second.

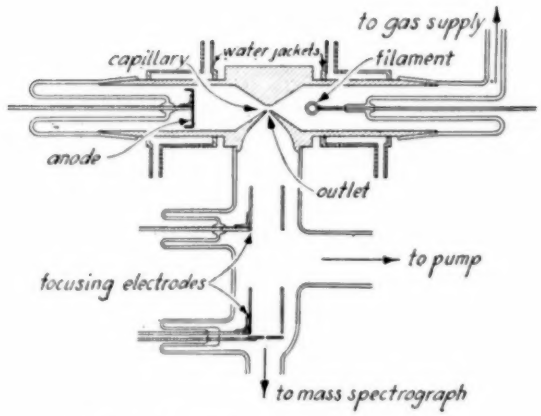

FIG. 1. Diagram of experimental tube.

In the first tube tested the ends of the two enclosures, instead of being conical as shown in the figure, were flat and the capillary, instead of being concentric with the two cylindrical enclosures, was on the bottom. In other words, the lowest generating line of the capillary was a continuation of the lowest generating lines of the two cylindrical enclosures. This design was adopted in order to minimize the distance between the outlet and the first high voltage electrode thus giving the most favorable arrangement for the initial focusing of the ion beam. Since no difficulty was experienced in initial focusing, and since the lack of symmetry in the position of the capillary made the starting of the discharge difficult, that design was abandoned in favor of the one shown.

In order to start the discharge the metal walls are connected to the anode through a resistance of from 20 to 30 thousand ohms. A low current discharge then starts in the cathode enclosure, the walls of the enclosure acting as anode. Electrons from this discharge are shot through the capillary and precipitate a high current discharge to the anode through the capillary. A symmetrical field about the end of the capillary is most favorable for shooting electrons through the capillary and thus for starting the main discharge. The symmetrical field also tends toward greater stability of the arc for, if any transients tend to extinguish the arc, it immediately starts again. As regards convenience in tube design, it seems safe to say therefore that wide variations are permissible provided the walls at the ends of the capillary are geometrically symmetrical and, of course, provided cathode and anode are not too far removed from the ends of the capillary.

Various different filaments were tried but the one finally adopted consisted of a 20-mil molybdenum wire about 6 inches long wrapped with 8-mil nickel. The resulting "piano wire" was wound on a 3/32-inch mandrel to form a helix. The emitting surface was a mixture of barium and strontium oxides. The molybdenum served as a heating element and the nickel as a binder for the oxides.

Several 1/4-inch holes (not shown in the figure) were drilled through the stainless steel block for water cooling and water jackets were provided for each of the two stainless steel tubes.

A number of different capillaries were tried ranging in diameter from 1.5 to 4.0 mm and in length from 4 to 20 mm. The difficulty in starting a discharge increased with increasing length and with decreasing diameter of the capillary. In some instances the discharge started as soon as the e.m.f. was applied and in others it was necessary to apply a "leak tester" to the glass on the anode side. In most of the tests an e.m.f. of 230 volts was used simply for convenience although arcs have been maintained easily with an e.m.f. of 115 volts. The arc drop ranged from 60 to 140 volts. In general, the arc drop is least for the capillary having the greatest diameter and smallest length. For any one discharge tube the arc drop is a minimum at some one pressure and rises gradually as the pressure is changed on either side of the minimum.

Measurements of the number of ions leaving the discharge per second through the outlet were complicated by space charge near the outlet and by the emission of secondary electrons from the electrodes in the high voltage tube. Ten kilovolts, applied to the first electrode, were usually sufficient to overcome the space charge near the outlet and thus give saturation ion current. With this voltage most of the ions went through the first electrode and were collected by the second. The resulting secondary electrons, emitted by the second electrode, were prevented from contributing to the measured ion current by means of a small retarding potential (45 to 350 volts) maintained between the two high voltage electrodes.

The ion current was measured for each discharge tube as a function of the variables in the arc proper. These were the arc current, the gas pressure, the potential of the steel walls with respect to the anode, and the previous history of the tube. A slit (5 mm long and 1.5 mm wide) in the bottom of the second high voltage electrode allowed a small fraction of the ions to enter a mass spectrograph (not shown in the figure). It was possible, therefore, to determine the nature of the ions in a sample of the beam as a function of the variables mentioned above.

Results and Conclusions

The current of ions leaving the discharge through the outlet depends upon the number of ions produced per second in the discharge and upon the electric field in the vicinity of the outlet. These two variables and the variables on which they in turn depend will now be considered.

The number of ions produced per second depends upon the current density and potential drop in the capillary and upon the concentration and nature of the gas present. Experimentally it was found that, with the metal walls floating or connected to the anode through a high resistance, the ion current (leaving the discharge through the outlet) for constant arc current varied over fairly wide limits, in most cases by a factor of two. When an arc was first started, the ion current was always low and increased with continued operation. Since there was no accompanying change in the *relative* numbers of ions of different masses collected in the mass spectrograph or of arc drop, it was concluded that the increase in current resulted from an increase in the current density in the capillary rather than from any change in the nature of the gas or drop along the capillary. The following is a possible explanation of the change. There are two possible paths through which current can flow from anode to cathode: the capillary, and the metal walls. The fraction of the arc current which follows the metal path (and thus produces no ions) is greater or less, depending upon the number of secondary electrons emitted by the walls of the anode enclosure. Continued operation of the discharge tends to remove surface films from the walls, thus reducing the number of secondaries emitted and forcing the arc current to take the path through the capillary. If the walls are made negative with respect to the cathode, electrons from the cathode are prevented from reaching the walls and thus most of the arc current must go through the capillary. This procedure does not result in any great increase in ion current for a given power input since the current resulting from the emission of secondaries from the walls of the anode enclosure must be supplied by the metal wall circuit. Reductions in the fraction of the arc current taking the metal path can be accomplished by selecting, for tube construction, a metal which does not emit many secondaries and by reducing to a minimum the area of metal exposed to the discharge on the anode side of the capillary.

Let us consider now the electric field in the vicinity of the outlet and its effect upon the ion current. In general a metal surface in contact with an ionized gas and negative with respect to it is covered with a positive ion space-charge sheath.[3] The thickness of the sheath increases with increasing negative voltage and with decreasing ion density. In the capillary, then, the region of ionized gas in the center is surrounded by a space charge sheath separating this region from the walls. The thickness of the sheath depends upon the ion density in the capillary and upon the potential of the central region with respect to the walls. Consider now ions from the discharge which leave the capillary through the outlet in the side of the capillary. If the thickness of the sheath is large in comparison with the diameter of the outlet, the outlet introduces no distortion in the sheath. Thus ions drifting into the sheath from immediately over the outlet suffer accelerations normal to the sheath and leave the discharge through the outlet. As the sheath thickness decreases, a depression develops immediately over the outlet. Ions which then drift into the sheath are accelerated in a diverging field and thus not all of them get through the outlet. If the sheath is extremely thin it bends around the edges of the outlet thus allowing a part of the discharge itself to stick out through the outlet, the ions being removed from this part of the discharge by the field in the high voltage

[3] Langmuir and Mott-Smith, G. E. Rev. **37**, 449, 538, 616, 762, 810 (1924).

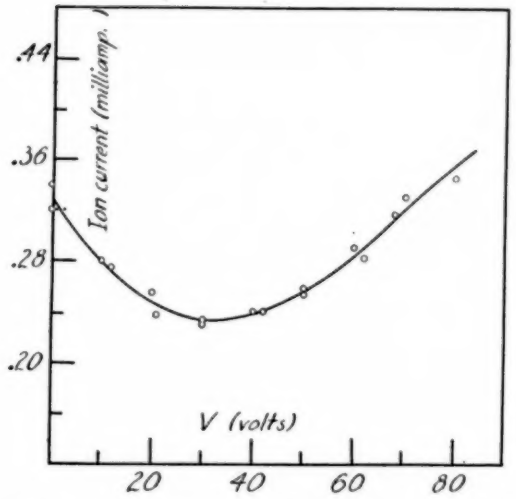

FIG. 2. Ion current *vs.* potential of the metal walls with respect to the cathode. Arc current 1 ampere, pressure 0.095 mm, capillary diameter 4 mm, and outlet diameter 0.83 mm.

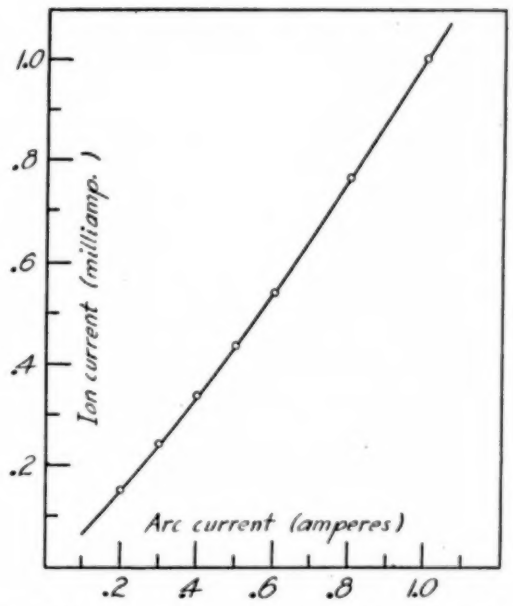

FIG. 3. Ion current *vs.* arc current with metal walls connected to anode through 20,000 ohms. Pressure 0.15 mm, capillary diameter 3.2 mm, and outlet diameter 1.2 mm.

tube. The fraction of the area of the outlet available for this "sticking out" of the discharge increases, therefore, with decreasing sheath thickness and thus, in this region, the ion current increases with decreasing sheath thickness for constant ion density. The correctness of this picture is indicated by the results presented in Fig. 2. In this figure the ion current is plotted as a function of the negative potential of the metal walls with the cathode as a fixed reference, other measurable variables remaining constant. As one would expect from the above picture, for high negative voltages, as the negative voltage and thus the sheath thickness increase, the ion current increases. In the intermediate region the ion current is low. As the sheath thickness decreases after having passed the minimum, the ion current again increases indicating a "sticking out" of part of the discharge through the outlet. It was not possible to extend this curve in either direction in search of a leveling off, since further increase in negative voltage put the arc out, and since any decrease made the walls positive with respect to the cathode, thus allowing electrons to reach the walls and complicating the interpretation of the curve. Maximum ion currents are obtained, therefore, either from a number of extremely small outlets or from one large one.

Fig. 3 is a plot of ion current leaving the discharge with arc current as the independent variable. If the effective area of outlet were constant, one might expect an approximate proportionality between ion current and arc current. But since the sheath thickness decreases with increasing ion density and thus with increasing arc current, the effective area of outlet is not constant. Since, in this case, the outlet was relatively large (1.18 mm in diameter) it is believed that the sheath was small by comparison and thus the effect of changing sheath thickness on outlet area was small, and thus the lack of any great curvature is taken as good evidence for a proportional dependence of ion current on arc current for constant outlet area.

A number of tests were made to determine the dependence of ion current and arc stability on gas pressure. Over the range from 0.035 to 1.0 mm no marked dependence of ion current on gas pressure was observed although it increased slightly with increasing pressure. In pure hydrogen, however, for pressures below 0.06 mm the arc shows a marked tendency to go out. A pressure of 0.1 mm is suggested, therefore, as a sufficiently high pressure to insure reliable operation. As far as the operation of the arc is concerned, it can be made stable at low pressures by introducing traces of impurities into the hydrogen although this is undesirable since under

these conditions an appreciable fraction of the ions are those of the impurity.

The design of capillary arc shown in Fig. 1 presents a different focusing problem from that usually encountered since there is no auxiliary electrode for drawing the ions out of the arc. In this problem there are two limiting cases: one in which the outlet diameter is large in comparison with the sheath thickness so that a part of the discharge actually sticks out through the outlet, and the other in which the outlet is small so that the ions are shot out by the potential drop in the sheath. In either case there is very little net space charge in the immediate vicinity of the outlet, for in the first case electrons drifting out of the discharge with the ions tend to neutralize space charge, and in the second not only does the smallness of the outlet reduce the number of ions but the sheath drop furnishes them with an initial velocity. Studies of focusing were greatly simplified by the fact that slight traces of gas in the high voltage tube rendered the beam sufficiently luminous to be clearly visible in a darkened room. With low voltage on the first high voltage electrode, the beam appeared to come from a rather large area indicating considerable spreading of the ions after leaving the outlet. As the voltage was increased, not only did this area decrease, but the ions continued to converge in their flight down the tube. With an ion current of 4.2 ma and a voltage of 10 kv the beam reached a minimum width of 12 mm at a distance of about one centimeter below the first high voltage electrode. Since this beam width was sufficiently small to allow the ions to pass through the first high voltage electrode, and since the work of Dr. Tuve and his collaborators[2] on further focusing was already so complete, these studies were not continued. It should be added, however, that the apparent beam edge was always extremely sharp. That this corresponded with the physical facts was shown by the sharp drop observed in the current collected by the first electrode when the beam appeared just to clear its edges. There are, therefore, certain advantages to be gained by allowing the ions to leave the discharge with negligible velocities and impart all of the energy in a region of relatively high vacuum. Under these conditions, one is not faced with the problem of refocusing an initial beam, heterogeneous in energy and direction, which comes from a region in which gas scattering is possible.

Studies of total ion current were, of course, complicated by the passage of part of the arc current through the metal and by the dependence of the effective area of the outlet on sheath thickness, as discussed above. The indications were, however, that the ion density, and thus the ion current for constant effective area of outlet, were approximately proportional to the current density in the capillary. With a 3.2-mm capillary and a 1.2-mm outlet, the ion current for a 1.92 ampere arc was 4.2 ma. Thus one may expect about 16 ma per square centimeter effective area of outlet for a current density of 1.0 ampere per square centimeter in the capillary. In the 3.2-mm capillary, the current density for a 1.0-ampere arc is about 12.5 amperes per square centimeter. Currents as high as 5 amperes have been passed through such a capillary, giving a current density of 62.5 amperes per square centimeter and thus an ion current density of 1000 ma per square centimeter. For the sake of comparison, the source described in the first reference gave 8 ma per square centimeter for a 1.0-ampere arc.

In Fig. 4 a fairly typical mass spectrograph curve is presented merely to show the positions and shapes of the various peaks. Although a number of complete curves were taken, in the interest of speed only the heights of the various peaks were recorded in most of the tests. In most of the tests taken with the mass spectrograph, the two high voltage electrodes and the mass spectrograph were 1160 volts negative with respect to the steel walls of the discharge tube. As can be seen, the diatomic and triatomic ions are in the majority, the relative magnitudes of the two peaks depending on the pressure, while the primary proton peaks are disappointingly low. With pure hydrogen, the fraction of the ion current carried by primary protons ranged from 5 to 20 percent, and was usually about 10 percent. No marked dependence, of primary proton percentage on the arc variables, was observed over the ranges of currents and pressures used although there was some slight indication of an increase with measured pressure. There was some evidence that the addition of helium to the hydrogen tended to increase the proton per-

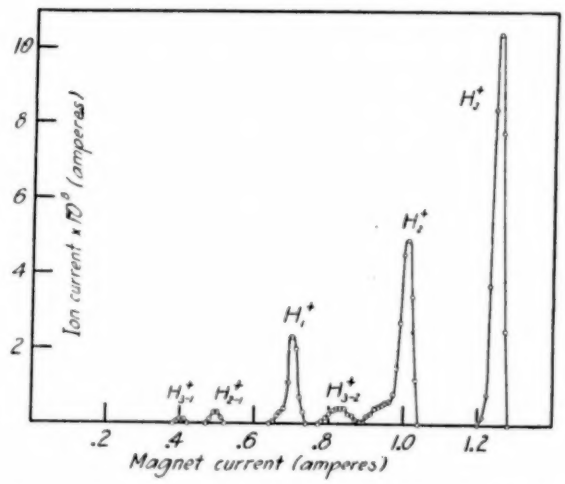

FIG. 4. Typical mass spectrograph curve. Pressure 0.13 mm.

centage, but the evidence was not conclusive and since the effect, if present at all, was small, only a few tests were made.

It was hoped that the mechanism employed by Lamar and Luhr[1] for producing protons might be of use in this type of ion source. Briefly, if both ions and neutral particles have a low accommodation coefficient, and if the walls are maintained highly negative, ions striking the walls rebound as neutrals retaining a large fraction of the energy gained in the negative potential drop. This energy going into the gas tends to increase its temperature. If the neutral particles also have a low accommodation coefficient large temperature differences are possible between gas and walls. With the gas at a high temperature, the hydrogen exists in the atomic rather than the molecular state and the ions are therefore protons. Tests on the capillary type source and further tests on the type described in the reference above confirmed the conclusion that extremely clean surfaces are required for the existence of low accommodation coefficients. This surface cleanness, although possible, requires care in technique which is hardly practical in a high voltage installation.

Some hope for increased proton percentages is offered by the fact that heavy ions at high speeds break up, on collision with gas molecules, into protons and neutral particles. That this occurs is indicated by the presence of peaks in Fig. 4 at 0.4 and 0.5 ampere magnet current. If these are protons, they appear with one-half and one-third energy as would be expected if they were formed by the break-up of H_2^+ and H_3^+, respectively. This conclusion is further substantiated by the fact that the relative heights of these two peaks vary in the same way as the relative heights of the H_2^+ and H_3^+ peaks. The peak at 0.8 ampere results from the break-up of H_3^+ ions to form H_2. It is possible, on knowing the relative heights of the various peaks, the pressure in the discharge tube, and the various dimensions of the apparatus, to get some idea of the efficiency of these break-up mechanisms, the only uncertainty being the angular distribution of the protons after break-up. A lower limit to the efficiency of break-up can be set by assuming no angular scattering. With this assumption, every heavy ion, which would have entered the spectrograph had it not been broken up, produces a proton which does enter the spectrograph. Knowing, then, the number of protons per heavy ion, the length of path in the discharge tube at constant potential, and the pressure in the discharge tube, one can calculate from these data the average number of collisions per centimeter path at normal pressure and temperature which result in break-up. This calculation gives, as a lower limit, for the H_2^+ five and for the H_3^+ two collisions per centimeter path at one millimeter pressure and room temperature resulting in break-up. As an extreme upper limit, one might assume that on break-up the protons are scattered equally in all directions. Knowing the solid angle subtended by the slit system of the spectrograph at any point along the path of the ion beam, one is able to perform the necessary integrations and solve for the efficiency necessary to account for the observed number of protons. This assumption leads to about 250 times as many collisions per centimeter path as the former one. A more reasonable assumption is that the protons are scattered as though they had collided as elastic spheres with spheres of equal mass. Since the resulting distribution gives four times as many protons scattered in the forward direction as the equal angular distribution, the ratio between upper and lower limits is now reduced to about 60. For 1160-volt ions, therefore, the number of collisions per centimeter path at normal pressure and temperature resulting in break-up lies some-

where between 5 and 300 for H_2^+ ions and between 2 and 120 for H_3^+ ions. These tests were not repeated for other voltages. However, the absence of marked broadening of the primary proton peak for high pressures, and negative voltages of the capillary walls as high as 180 volts, indicated that the efficiency of break-up must be extremely small for voltages less than 180.

The possibility of using the break-up mechanism for producing protons depends, of course, upon the relative importance of scattering in removing ions from the beam as it passes through the gas. In order to test this an additional electrode was introduced 4.0 centimeters below the outlet to the tube. It consisted of a cylinder 1.0 centimeter in diameter and 4.0 centimeters long with a plate extending from the upper edge of the cylinder radially to the glass walls of the discharge tube thus sealing this region from the region of high vacuum. Previous tests, without the additional electrode, having shown little change in total ion current with pressure, it was assumed that, with the additional electrode any decrease in ion current with increasing pressure resulted from scattering in the region between outlet and additional electrode. The measurements indicated an approximate exponential dependence of ion current on pressure as would be expected from loss due to scattering. The loss for a gas path equivalent to 1 mm at 1 mm pressure was 3/4 of the current in the beam. With this gas path the fraction of primary protons increased to 30 percent. These were definitely primary protons from the discharge since they possessed the full energy and their high percentage merely showed preferential scattering of the heavier ions. In all of the tests with the additional electrode, the maximum current was realized with a potential of about 3 kv on the electrode, showing for lower voltages an underfocusing and for higher an overfocusing of the ion beam.

Since the angular distribution of the protons after formation from the break-up of heavier ions is not known it is not possible at the present stage to give an accurate estimate of the ultimate limit to the total proton current. However, a few remarks as to the directions in which to proceed in designing a "break-up" region seem to be in order. The design of such a region presents two problems: that of breaking up the ions and of focusing the resulting protons. The first of these problems is relatively simple. One needs, simply, to give the ions an energy of 1 kv or more and to have sufficient gas present to insure the desired number of break-up collisions. In order to focus the protons the field in the break-up region should be strongly converging so that scattered ions may be drawn back into the ion beam. The region should be wide in comparison with its length so as to provide the field with ample opportunity to act on the ions before they reach a wall and are lost. In the source described by Tuve and his collaborators[2] some of the lines of force from the auxiliary electrode pass through a constriction, separating this electrode from the discharge, and up into the capillary. This arrangement provides a converging field in a region of reasonable gas pressure, but the voltage drop in this leakage field is necessarily low since high voltages here extinguish the arc. Since the efficiency for break-up with low voltages is small, few protons are produced in this region. It seems more advisable, therefore, to get the ions completely out of the discharge, possibly by one of the mechanisms outlined above, and then provide them with the necessary energy in the region of gas. The outlet to the break-up region should be a hole in a diaphragm rather than a long tube since the angle spread of the beam leaving this region is probably large. A discussion of the relative merits and demerits of diaphragms as compared with tubes is given in the second reference. Although the "break-up" mechanism for forming protons has with it the undesirable feature of gas scattering which makes focusing difficult, it does not make focusing impossible and seems to offer the most promising means of obtaining high proton yields.

In conclusion, the authors wish to express their indebtedness to Mr. Walter Kallenbach, head of the Physics Shop, whose advice in design and whose cooperation in execution made possible the testing of a large number of tubes. We wish also to thank Dr. C. M. Van Atta for his excellent suggestions and advice during the preparation of the manuscript.

Polymorphism, Principally of the Elements, up to 50,000 kg/cm²

P. W. BRIDGMAN, *Research Laboratory of Physics, Harvard University*

(Received September 26, 1935)

A new technique is described by which pressures of 50,000 kg/cm² and more may be applied to solids, and the parameters of any transitions measured. A systematic examination has been made for polymorphism of many of the elements in the new pressure range. New modifications are found for Bi, Hg, Tl, Te, Ga, and I_2, and the transition parameters measured. A beginning has been made of a systematic study of polymorphism of compounds, and results obtained for KCl, KBr, and KI, which assume at about 20,000 kg/cm² presumably the CsCl type of structure.

THE NEW TECHNIQUE

HITHERTO nearly all my high pressure measurements have been restricted to a range of about 20,000 kg/cm², and by far the larger part have reached only 12,000. The limit has been set by the bursting strength of the cylinders. By subjecting the cylinders to an initial stretching considerably beyond the elastic limit it is possible to put them into such a state of internal stress that the best grades of steel will withstand pressures of the order of 40,000 kg/cm². but the benefit of any such treatment rapidly tapers off with time, so that 20,000 is as high as I have found it profitable to go, and even then rupture is frequent. The practical limit of the pistons with which pressure is produced is considerably higher, around 40,000 kg/cm².

It is evident, and in fact a number of persons have independently made the suggestion to me, that it would be ideally possible to reach any pressure whatever by making a nest of pressure apparatuses, one within the other, each inner apparatus being exposed to a uniform hydrostatic pressure all overexerted by the next outer apparatus. The extreme mechanical difficulty of carrying out this idea, even in an apparatus of only two stages, has hitherto deterred me from any such attempt at extending the pressure range. It is quite conceivable, however, that it would be possible to accomplish the desired end by subjecting the internal apparatus to a less complete support than would be afforded by a hydrostatic pressure all over its external surface. Such, has in fact, proved to be easy, and in the following results are given for a large number of routine experiments made with such an apparatus up to 50,000 kg/cm².

The cylindrical vessel exposed to internal hydrostatic pressure may be supported with sufficient effectiveness by applying an external pressure to the curved surface only of the cylinder. A very simple calculation by elasticity theory shows the effectiveness of such support. Consider, for example, two cylinders both initially of the same internal diameter, one with infinitely thick walls, and the other with an external diameter four times the internal diameter. To the first cylinder is applied a certain pressure, and to the second cylinder the same pressure and at the same time an external pressure equal to one-half the internal pressure. Calculation by the conventional formulas, as for example in Love's *Elasticity*, shows that the radial stretch at the inner surface of the second cylinder is only 0.28 as great as that of the first. A factor so advantageous as this cannot be gained by cold working. If the ratio of external to internal pressure could be automatically maintained in some way as the internal pressure increases, the second cylinder could obviously be carried to a much higher pressure without rupture than could the first cylinder with its infinitely thick walls.

A simple scheme by which the external pressure may be automatically maintained at a predetermined fraction of the internal pressure is illustrated in Fig. 1. The external walls of the cylinder are given a conical shape like a stopper, and this steel "stopper" is pushed into an external sleeve by the same force with which the piston is driven into the cylinder, compressing the material within it. The friction on the walls of the cone is of course a complicating factor that must be allowed for empirically, but by using carefully polished surfaces, and a graphite and vaseline lubricant the purpose is accomplished with about the proportions shown, and

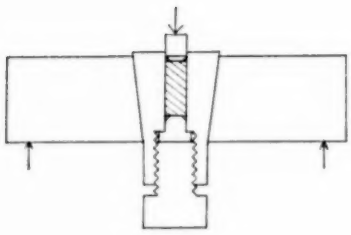

FIG. 1.

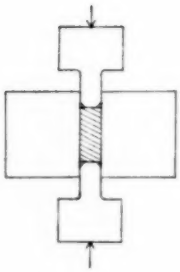

FIG. 2.

FIG. 1. Illustrates the new arrangement by which an external pressure is automatically applied to keep pace with the internal pressure. The diagram is approximately to scale; the diameter of the "stopper" at the upper end is 2.5 cm.

FIG. 2. The double ended cylinder and pistons by which the transitions of bismuth were measured.

the stopper comes back out of the sleeve without sticking on release of pressure.

As already stated, with this arrangement many routine measurements have been made to 50,000 kg/cm². The weak part of the apparatus is now the piston, 50,000 being beyond the reach of any steel that I have been able to find. Fortunately carboloy, the recently developed cemented carbide of tungsten and cobalt, turns out to have a much higher compressive strength than the hardest steel, and 50,000 kg/cm² or even considerably more may be easily reached with it; I am exceedingly indebted to Dr. Zay Jeffries of the Carboloy Company of America, through whose kind offices I was presented with sufficient carboloy in the form of rods about 6 mm in diameter to make 100 pistons 6 mm long. It is usually possible to use a single piston for half a dozen excursions to 50,000 kg/cm² before it breaks.

Full details of the apparatus are deferred to another paper, only a few of the more important points will be mentioned here. The simple apparatus sketched in Fig. 1 is evidently capable of yielding quantitative information about polymorphic transitions by merely determining the position of the piston as a function of pressure, which is exactly the method used in my former work at lower pressures. It is probable that the apparatus can also yield information about compressibility, although this second use has not been seriously attempted yet. There will obviously be complications because of hysteresis and friction, which, however, I believe can be overcome. In any event, the accuracy cannot be as high as in my previous work, in which pressure is truly hydrostatic and is transmitted by a true liquid. But such experiments are no longer possible at ordinary temperatures at pressures as high as this, for nearly everything freezes to the solid. The substance which would longest resist freezing is doubtless helium; Simon's[1] extrapolation indicates that even it will freeze at room temperature at a pressure in the neighborhood of 100,000 kg/cm², a pressure which I have actually reached under special conditions on one occasion. It has been a suprise, however, to find that the apparatus is capable of accuracy not much lower than that of the former apparatus, as has been established on several occasions when measurements of the same transition have been made with the two types of apparatus. In any event, the field is sufficiently new, and the results to be expected of sufficient interest to justify the use of methods not of the highest accuracy.

One reason that the pressure fails to be truly hydrostatic arises from the friction exerted on the walls by the material undergoing compression as it moves down into smaller volume. If the ratio of length to diameter is high, enormously high friction may be developed in this way, so that the pressure at the lower end may be only a small fraction of the pressure immediately under the piston. In this apparatus the dimensions were such, however, 6 mm diameter and length of the order of 9 mm, that the friction could not be an important fraction of the mean hydrostatic pressure. The friction is less when soft materials are used, because of their low plastic limit, and it is this kind of material that has been used in most of these investigations. Harder materials can be experimented with by embedding them in a sheath of some softer material, such as lead or even copper. Such a sheath becomes a positive necessity for many materials, particularly above 100°. In my early work I had found that mercury amalgamates and breaks the cylinder at a few thousand kilograms pressure. Action quite similar to this takes place with many of the low melting metals at these new higher pressures. Sodium, for example,

[1] F. Simon, M. Ruhemann and W. A. M. Edwards, Zeits. f. physik. Chemie **B6**, 62 (1929).

cannot be used directly in contact with steel at any temperature, but alloys with it and ruptures it. Tin, bismuth and others act similarly. Also such substances as sulfur attack chemically the steel, which must be protected from direct contact.

In addition to the friction of the material under compression, there is also considerable friction at the closure under the piston, which is an arrangement utilizing a conical ring as shown. The effect of both sorts of friction was eliminated from the transition pressure by taking mean values obtained with increasing and decreasing pressure. One serious result of the very considerable friction, however, was loss of sensitivity; a number of substances were found to have probable transitions by a shearing method, described in a previous paper, but showed nothing large enough to be measurable by this direct volumetric method.

Temperature control was effected through a temperature bath, which consisted of a pan soldered to the conical supporting sleeve. Solid carbon dioxide temperatures were easily reached in this way, and by means of an electric heater in oil, temperatures up to the softening point of the steel were reached. 200°C was about the limit for measurements to 50,000; at higher temperatures the cylinder softens perceptibly, as does also the carboloy piston, which seems to be notably stronger at the lower temperatures.

The detailed results now follow. First are given those elements for which it has been possible to carry through a full determination of all the thermodynamic parameters, namely, transition pressures and accompanying change of volume as a function of temperature. Next those elements are enumerated for which negative results were found, with a list repeated for the sake of completeness from a previous paper of those elements which the shearing method has shown to be probably polymorphic. Finally are given the transition parameters for the potassium halides, with a mention of other exploratory work for a few simple compounds.

Detailed Results for the Elements

Bismuth

This metal was found to be polymorphic at high pressures over a year ago, and part of the results have been already summarized in print.[2] The first work with bismuth was done with a different type of apparatus from that described above, not capable of nearly such high pressures, but of sufficient usefulness to justify a brief description. In general idea it is not dissimilar from a method used by Tammann.[3] The method is sufficiently well indicated in Fig. 2. The bismuth is contained in a short cylinder, and compressed from both ends by two pistons pushed together by a hydraulic press. By the use of two pistons friction is very materially reduced, and the sharpness of the readings increased. Mechanical stability is increased by the large ends shown on the pistons. The cylinder is made of "Solar" steel; this is a water hardening silicon-manganese steel of very materially higher tensile characteristics than the chrome-vanadium steel used hitherto in my work. In fact, it was the availability of this new grade of steel that gave the impetus to all this attempt to reach higher pressures. The solar steel cylinder of Fig. 2 was treated by an initial stretching exactly as my former cylinders. Temperature was varied by means of a heating coil wound over the outside of the cylinder. With this arrangement measurements could be made up to 30,000 kg/cm² or perhaps more.

With this first apparatus two new high pressure forms of bismuth were discovered, and measurements were made on the transition lines I–II and II–III between 79° and 182°C. At 197° the pressure of the melting of I was located, 15,700 kg/cm², increasing pressure from the domain of the solid to that of the liquid. The pressure found in this way agreed well with the pressure extrapolated from former measurements up to 12,000. The melting pressure had not been held for longer than two minutes, however, when the cylinder broke, amalgamated by the liquid bismuth; the amalgamation was very obvious in the fracture.

With the "stopper" apparatus an exploration was made for other modifications at still higher pressures. The I–II and II–III transitions were first located at 134° and the change of volume determined. At somewhat less than 30,000 at

[2] P. W. Bridgman, Phys. Rev. **47**, 427 (1935).
[3] G. Tammann, Zeits. f. anorg. u. allgem. Chemie **199**, 209 (1931).

this temperature the cylinder broke, amalgamated by the solid bismuth. The changes of volume and also the transition pressure so found agreed well enough with the values obtained with the first apparatus. A new cylinder was now used and the bismuth enclosed in a copper sheath. This was successfully carried to 50,000 at 20°. At the upper end of the pressure range there was considerable plastic yield of the cylinder, so that a small transition might have escaped notice. On release of pressure, a very small discontinuity in the volume of not more than 5 percent of the volume change of the other transitions was found near 40,000. No special significance was attached to this at the time. But on making shearing measurements with the apparatus described in the previous paper, there appeared unmistakable evidence that this discontinuity must have been really a transition. The experiment was then repeated with two different set-ups of the "stopper" apparatus at −79° and 0°C. On each occasion the break was found with decreasing pressure and there seems no doubt of the reality of the transition. The "region of indifference" of this transition unfortunately appears to be rather wide, the transition occurring with increasing pressure so near to 50,000 that it is obscured by volume creep in the cylinder. It was therefore not possible to determine the average of the transition pressure with increasing and decreasing pressure, so that the true transition pressure is restricted to a much broader region of uncertainty than is usually possible. The width of the band of indifference did not seem to be importantly less at 20° than at −79°, and for this reason the attempt was not made to get more accurate values by increasing the temperature, a procedure which would ordinarily be effective, but here would have been of doubtful value because of the rapid increase of plastic creep with higher temperatures. The volume change was so small that it could be determined with only small accuracy; the actual value found at −79° was a little more than one-half that at 20°.

At solid CO_2 temperature the two transition points I–II and II–III are so close together that it was not possible to separate them. The total change of volume, I–III, found at this point was 0.0073, which agreed exactly with the sum of the values for I–II and II–III extrapolated from readings at higher temperatures. In view of the breaking of the cylinder when melting of I took place, no attempt was made to obtain points on the melting curves of II or III. The parameters at the triple points given in Table I were obtained by calculation. The parameters for the melting of II and III are very rough, since they involve extrapolations and the difference of nearly equal quantities. The parameters of the transition III–IV given in the table are also very rough.

The transition parameters are collected in Table I, and the phase diagram is shown in Fig. 3 and the changes of volume in Fig. 4. It will be seen that there is a rough analogy between the phase diagram of bismuth and that of water, which possibly may be of significance.

Mercury

The transition was first found at CO_2 temperature at about 14,000 kg/cm². The mercury

TABLE I. *Transition parameters of bismuth.*

PRESSURE (kg/cm²)	TEMPERATURE (°C)		$\frac{d\tau}{dp}$	Δv (cm³/g)	LATENT HEAT (kg cm/g)	(g cal./g)
			LIQUID–I			
1	271.0		−0.00342	0.00345	−549	−12.87
5,000	251.9		418	386	485	11.37
10,000	228.8		506	419	416	9.76
15,000	200		61	440	346	8.11
			I–II			
18,000	170		−.196	−.00480	108	2.53
19,000	150		−.196	485	104	2.44
24,100	50		−.196	475	78	1.83
29,200	−50		−.196	455	51	1.20
			II–III			
22,800	170		−.298	−.00300	44₅	1.04
23,600	150		−.298	.00310	44	1.03
26,900	50		−.298	.00310	33	.77
30,300	−50		−.298	.00275	20	.47
			III–IV			
43,000	−100		+.3(?)	−.0003(?)	−.2(?)	−.0047(?)
43,500	+ 50		+.3(?)	.0004(?)	.4(?)	−.0094(?)
			APPROXIMATE TRIPLE POINTS			
			L–I–II			
17,300	183	L–I	−.0066	.0045	−310	−7.27
		I–II	−.196	−.0047	110	2.58
		L–II	+.00046	−.0002	−200	−4.69
			L–II–III			
22,400	185	L–II	+.0004(?)	−.0002(?)	−200(?)	−4.69(?)
		II–III	−.298	−.0029	45	1.05
		L–III	+.0091(?)	−.0031(?)	−155(?)	−3.64(?)
			I–II–III			
32,300	−110	I–II	−.196	.0043	36	.84
		II–III	−.298	.0025	14	.33
		I–III	−.221	.0068	50	1.17

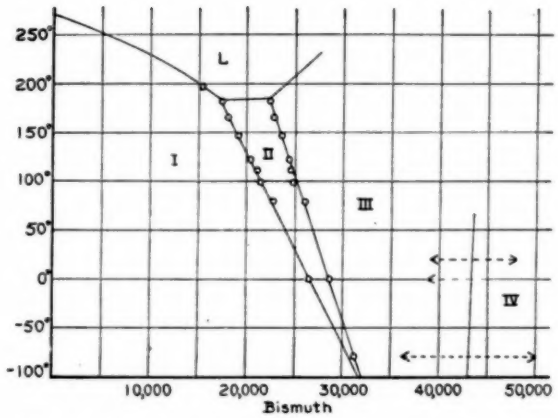

FIG. 3. The phase diagram of bismuth, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate. The arrows on the transition line III–IV mark the limits of indifference.

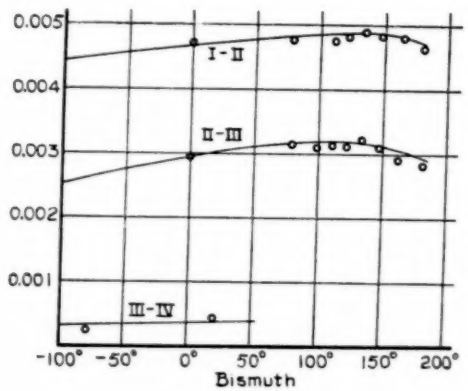

FIG. 4. The volume changes for the various transitions of bismuth, temperature in degrees Centigrade as abscissa against volume change in cm³/g as ordinate.

was frozen directly into the apparatus without protecting sheath. Determinations at this temperature were made with increasing pressure, decreasing pressure, and then with increasing pressure again. Temperature was then raised to 0°C and the pressure to about 36,000 to maintain the mercury solid, and the transition located with decreasing pressure. The run was terminated by leak of liquid mercury past the piston due to melting, in spite of the fact that the pressure in the apparatus was well above the melting pressure at this temperature. The change of volume of the transition was moderately large, corresponding to the total volume decrement produced by an increase of pressure of about 2000 kg, but nevertheless it was not sufficiently large. In conjunction with the super- and sub-

TABLE II. *Transition parameters of mercury.*

Pressure (kg/cm²)	Temperature (°C)	$\frac{d\tau}{dp}$	Δv (cm³/g)	Latent Heat (kg cm/g)	(g cal./g)
10,000	−109	0.0077	0.00104	22.1	0.518
15,000	− 73	67	.00071	21.1	.495
20,000	− 43	57	51	20.6	.483
25,000	− 17	48	41	21.8	.511
30,000	+ 5	40	36	25.0	.586
35,000	+ 23	32	32	29.6	.694

pressing which the transition will support, it was not found possible to land exactly on the equilibrium pressure, but the transition, when it started, always ran to completion. The apparatus was then set up again, and the measurements at −79° repeated, with good checks for both pressure and change of volume. Temperature was then raised to −43°, where it was maintained constant by continual manual manipulation by two assistants. After determination of the transition parameters from above and below, temperature was raised to +22°, and again two determinations made. No attempt was made for higher pressures because there was slight leak due to melting at +22°. At room temperature no other transition was found up to 45,000. A notable feature was the very markedly lower compressibility of the high pressure modification. The transition parameters are given in Table II, and the experimental points are shown in Fig. 5.

Extrapolation of the transition curve to atmospheric pressure suggests that the transition should run in the neighborhood of liquid-air temperature. Such a transition has not been reported, but should now be searched for. There are measurements of the x-ray structure down to liquid-air temperature; the best recent work is in accord about the structure and finds no change with temperature. There was an early determination that gave a discordant structure, but apparently even this cannot be explained in terms of a transition. In all these x-ray determinations the mercury was, of course, frozen at a higher temperature and then cooled to liquid-air temperature; under these conditions the transitions may have been suppressed, even if the temperature of the transition had been slightly exceeded, because of viscous resistance to the transition at low temperatures. If the mercury is cooled sufficiently beyond this temperature, however, the transition should run. There are

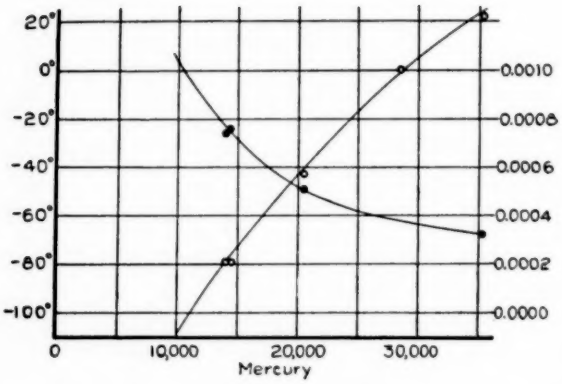

FIG. 5. The phase diagram and the volume change of the transition of mercury. Pressure in kg/cm² as abscissa, against temperature in degrees Centigrade as left-hand ordinate scale, and volume change in cm³/g as right-hand ordinate scale. The pressure-temperature points are shown as open circles, and the volume changes as filled-in circles.

measurements of the specific heat and the electrical resistance of mercury all the way from hydrogen temperatures. For the specific heat there are measurements by Simon[4] and by Pollitzer.[5] The measurements of Simon are very much the smoother; if these are plotted against temperature a very distinct break in the tangent will be found between 53° and 68°K. Simon does not comment on this, but it seems to me too pronounced to be spurious, and may perhaps be evidence of the transition. The resistance of mercury has been carefully measured at Leiden;[6] there is a gap in the temperature range from −156° to −183°. If the deviations from linearity of resistance as a function of temperature are plotted, a break will be found in this temperature interval, which again appears to be beyond experimental error. However, I do not regard this as definite as the specific heat evidence.

There is another consideration; it is possible that the transition curve found above does not extend all the way to atmospheric pressure, but it might be terminated by a triple point with still another modification somewhere below −79°, and with a low temperature transition line running steeply enough not to cut the temperature axis at atmospheric pressure. Such a state of affairs would demand the existence of yet another transition line, with a transition pressure at room temperature somewhere between 35,000 and the melting pressure, 12,000. Such a transition could not be observed at room temperature with the 50,000 apparatus because of leak, and certainly has not been observed with my other pressure apparatus. But at lower temperatures such a transition should be observable with the former apparatus. Accordingly a special examination was made for a new transition at −79° with the regular 12,000 apparatus. Pressure was now transmitted with a true liquid, and the indications were very much more sensitive than with the 50,000 apparatus. No transition was found up to 10,000 kg/cm². It therefore seems to me highly probable that the transition curve discussed above extrapolates to atmospheric pressure, and if the transition is not entirely suppressed by viscosity it will be found at atmospheric pressure not far from liquid-air temperature.

[4] F. Simon. Ann. d. Physik **68**, 241 (1922).
[5] Pollitzer, Zeits. f. Elekchemie u. angew. physik Chemie **19**, 513 (1913).
[6] Onnes and Holst, Comm. Phys. Lab. Leiden, No. 142a, 1914.

Thallium

The material was some which I had inherited from the late Professor T. W. Richards, and had been highly purified. Four different set-ups were used. In the first two the thallium was allowed to come directly in contact with the steel. The first run gave successful readings at 0° and 35°, reaching at 0° a maximum pressure of 51,000. There is a high pressure transition; the band of indifference is fairly wide, and although it was possible to locate the beginning of the transition with increasing pressure it was not possible to get a good value for Δv with increasing pressure, because it is obscured by plastic yield in the cylinder. The second set-up gave good readings at CO_2 temperature, and again Δv only with decreasing pressure. At 0° the run was terminated by the thallium blowing out past the piston. The third set-up gave good readings at 0° and 75°, the transition having become so sharp at 75° as to give good values for Δv both with increasing and decreasing pressure. At 180° the cylinder broke, amalgamated by the thallium, at a pressure which later proved to be almost exactly a transition pressure. It has been my rather common experience that rupture due to the

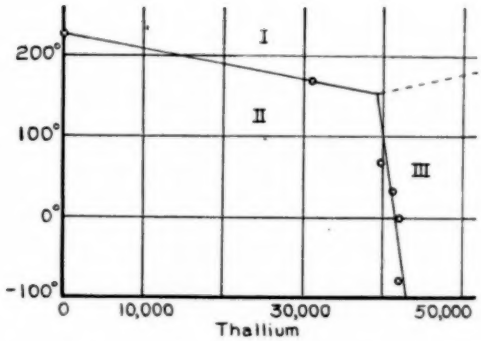

FIG. 6. The phase diagram of thallium, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate.

amalgamation effect is quite likely to take place while a transition is in progress; perhaps there is greater mobility during the transition, or perhaps the new phase has an intrinsically greater penetrating effect. The fourth and last set-up was with the thallium completely surrounded with a copper capsule to protect the steel. With this set-up a point was successfully determined at 170°, which proved, however, on plotting to have both too low a pressure and too low a change of volume to fit in with the other points. Thallium is known to be polymorphic at atmospheric pressure, and the transition line has been followed by Werner[7] up to 3000 kg/cm². This transition is of the abnormal ice type, temperature falling with increasing pressure. My point at 170° fits almost exactly on a linear prolongation of Werner's curve, and there can be little doubt but that this is the transition I–II.

TABLE III. *Transition parameters of thallium.*

PRESSURE (kg/cm²)	TEMPERATURE (°C)	$\frac{dT}{dp}$	Δv (cm³/g)	LATENT HEAT (kg cm/g)	LATENT HEAT (g cal./g)
		I–II			
1	227	−0.00187₅	0.00004₄†		
39,000	153		.00024	−41.7	−0.98
		II–III			
43,000	−100	− .0632	−.00039	+ 1.1	+ .026
39,000	+153		−.00053	+ 2.7	+ .063
		I–III*			
39,000	153	+ .00242	−.00029	−39.0	− .91

* The parameters for I–III are at the triple point I–III and are calculated.
† Werner's value.

[7] M. Werner, Zeits. f. anorg. Chemie **83**, 275 (1913).

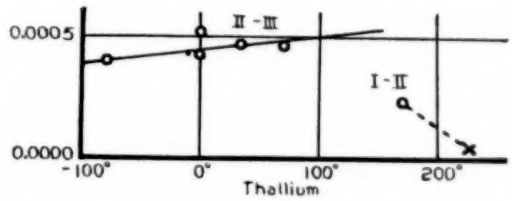

FIG. 7. The volume changes for the transitions of thallium, temperature in degrees Centigrade as abscissa against volume change in cm³/g as ordinate. The point at 227° for the transition of I–II is the value of Werner.

The phase diagram demanded by these considerations is shown in Fig. 6, and the changes of volume in Fig. 7. The II–III line, obtained by calculation from the thermodynamic parameters which are given in Table III, is shown dotted. At 170° the I–III transition was not found up to 45,000; this maximum at this temperature was set by plastic yield in the cylinder. It will be seen that this is consistent with the calculated I–III line.

Thallium was also examined by the shearing stress method at room temperature. The shearing strength curve has marked changes of direction in it, and there can be no doubt of the existence of other forms. It is not easy to determine from the shearing curve alone, however, whether the proper interpretation of it is one or two transitions. If the results of this volumetric analysis are accepted as meaning that there cannot be more than one transition, then the shearing experiments give 25,000 for the mean pressure of the transition. This is much lower than the value found above, and indicates an unusually large displacement of transition pressure by shearing stress.

Tellurium

The material was obtained from Kahlbaum; it was formed into a single crystal by my method of slow solidification, which should have effected an additional purification. This substance has a transition at room temperature in the neighborhood of 45,000 with a very large volume change, and at lower pressures probably another transition with volume change so much smaller that there is not complete certainty about it. Runs were made with three different set-ups. The first showed no transition to 52,000 at CO_2 temperature. A transition with unusually large volume

change was then located at 41,000 at 145°, but the volume change was not measured. The volume change was so large that it was easy to obtain pressure readings on the two-phase system. At 90° the experiment was terminated at 47,000 by fracture of the piston before the transition had put in an appearance. The second set-up gave at 171° an equilibrium point at 41,000. By cautious manipulation, what appeared to be a satisfactory value for the change of volume was also obtained at this temperature. The difficulty is that because of indifference and friction the transition runs to completion only at pressures very near the maximum attainable with the apparatus. At 142° a good value was obtained for the equilibrium pressure, but the indifference and friction were here so much greater that the piston was fractured in trying to force the reaction to run to completion in order to determine Δv. All the behavior at high pressure apparently indicates that we are here dealing with a transition much like that between ice I and III. That is, there is very little latent heat, and the transition may run with almost explosive rapidity at high temperatures, but there is an enormous temperature coefficient of transition velocity, so that at lower temperatures the transition will not run perceptibly under practical conditions.

After the measurements just described, explorations were made with the shearing apparatus at room temperature; this gave large and striking breaks, the only interpretation of which seemed to be two transitions. It is highly probable that the transition at the higher pressure, near 50,000, is the transition described above, the viscous resistance at room temperature being overcome by the shearing forces, as is not unusual. The transition at lower pressures seemed new. The volumetric apparatus was accordingly set up again, this time with the tellurium enclosed in a tin sheath, not to protect the steel, which was not necessary because there seems to be no chemical attack, but to reduce friction, which is unusually great with tellurium and makes the results somewhat irregular. At room temperature a doubtful transition with volume change near the limit of the detectible was found with increasing and decreasing pressure at a mean pressure of 36,000. At 85°, doubtful results were

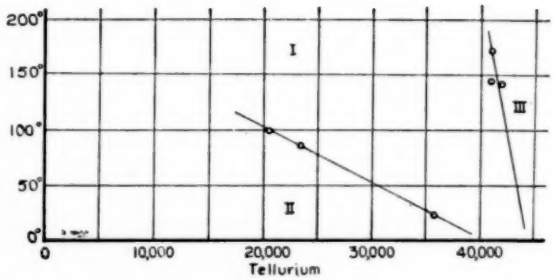

FIG. 8. The phase diagram of tellurium, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate.

again obtained, the readings during increasing pressure being obscured by an effect which later proved to be due to slight leak of the tin. The results at 100° of the original set-up were now reexamined, and a slight break found at a pressure which extrapolates linearly from the two just found. I therefore think that the location of this transition is established sufficiently well to justify putting it in the phase diagram, but it must be remembered that it is not entirely free from doubt. The Δv values are too uncertain to more than estimate; they cannot be much larger than 0.0001 cm³/g.

The transition parameters are indicated with sufficient accuracy in Fig. 8. In addition to the pressure-temperature values shown there, Δv II–III at 171° is 0.0058 cm³/g.

Gallium

A high pressure transition would be expected here for the same reason as for bismuth, namely, because the melting curve is of the ice type. The transition was at once found at CO_2 temperature at about 20,000; the change of volume is large, readings are easily made with the two phases present, and repetition gave good checks. Two other points were then obtained at $-41°$ and $-11°$. No other transition was found to 46,000. The transition line is of the ice type and intersects the extrapolated melting line only slightly beyond the limit of my previous measurements.[8] It was tempting to try for points on the melting line of II; this was not possible with the 50,000 apparatus, but the pressures are so low as to be within the reach of previous types of apparatus. A special cylinder was therefore con-

[8] P. W. Bridgman, Proc. Am. Acad. **56**, 104 (1921).

structed, much like that used in my measurements on the alkali metals to 20,000, only somewhat smaller. I was fortunate to obtain from Dr. W. M. Craig a supply of 16.5 grams of highly purified gallium. With this, measurements were made with the new apparatus by the conventional piston displacement method, pressure being transmitted by isopentane, and measured by a manganin pressure gauge in the liquid, so that all frictional effects were eliminated.

A large number of readings were made with the special apparatus. At first there appeared to be certain very puzzling inconsistencies. The explanation was presently found to be that there is still another high pressure modification, II′, very much like II in its thermodynamic properties, but totally unstable with respect to it. Points were obtained on both transition lines I–II and I–II′, but only on the one melting line L–II′. The points on the melting line were obtained by the procedure of raising temperature at constant volume. The reason for this was that the preliminary, and as it later proved, incorrect values for the change of volume on melting led to the expectation that this melting line would be nearly horizontal, and in this case the ordinary procedure would have been useless. The procedure of changing temperature gives much less accurate values than the other. The values so obtained checked within the expected accuracy with the values calculated from the data for the other transitions, so that it did not seem worth while to repeat for the improvement in accuracy that could doubtless have been obtained by the other method. Although no points were obtained on the L–II line because of some caprice with which the phases appeared, the existence of a melting line lying higher than L–II′ was checked on one occasion by carrying the solid phase II a degree or more above the melting temperature of II′ without melting. In view of the fact that a solid practically never superheats, this constitutes almost a certain check of the explanation in terms of a third absolutely unstable phase.

Advantage was taken of the opportunity to measure the changes of volume on the melting line of I, thus making possible a calculation of its thermodynamic parameters. This had not been previously possible because the quantity of gallium then available was too small. Over the first 6000 kg the new determinations of the melting temperature of I as a function of pressure agree almost exactly with the former values, but above 6000 the new temperatures are somewhat lower, the maximum difference being 1° at 12,000.

The results are shown in Figs. 9 and 10, and the parameters of the transition are collected in Table IV. The value for Δv at atmospheric pressure shown in Fig. 10 is the value of Boyer, 0.00529 cm³/g; it is seen to lie almost exactly on the curve with my high pressure values. No parameters are given in the table explicitly for the melting of II and II′ except at the triple points; experimental accuracy did not justify the attempt to estimate the variation of these parameters along the melting lines. The initial calculated slopes of these lines are indicated with sufficient accuracy in the figure.

Gallium is only the second example I have encountered in which a totally unstable phase appears at high pressures. The other example is water (both H_2O and D_2O). Perhaps it is significant that in both these cases the ordinary melting curve is of the ice type.

TABLE IV. *Transition parameters of gallium.*

Pressure (kg/cm²)	Temperature (°C)		$\frac{dT}{dp}$	Δv (cm³/g)	Latent Heat (kg cm/g)	Latent Heat (g cal./g)
			L–I			
1	29.85		−0.00205	0.00529	−782	−18.3
2,000	25.7		210	555	790	18.5
4,000	21.5		215	585	803	18.8
6,000	17.1		221	625	822	19.2
8,000	12.6		234	665	813	19.0
10,000	7.7		252	705	785	18.4
12,000	2.5		270	740	755	17.7
			I–II			
12,230	0		− .0085	− .0098	+314	7.4
14,580	−20		− .0088	98	281	6.8
16,800	−40		− .0095	98	240	5.6
18,800	−60		− .0108	98	193	4.5
20,500	−80		− .0130	98	145	3.4
			I–II′			
12,800	0		− 0.0852	− .0098	+314	7.4
13,390	− 5.0			—	—	
			Triple Points			
			L–I–II			
12,050	2.4	L–I	− .00270	.00740	−755	−17.7
		I–II	− .00852	− .0098	+317	+ 7.4
		L–II	+ .00151	− .0024	−438	−10.3
			L–I–II′			
12,750	0.4	L–I	− .00277	.0075	−740	−17.3
		I–II′	− .00852	− .0098	+314	+ 7.4
		L–II′	+ .00137	− .0023	−426	− 9.9

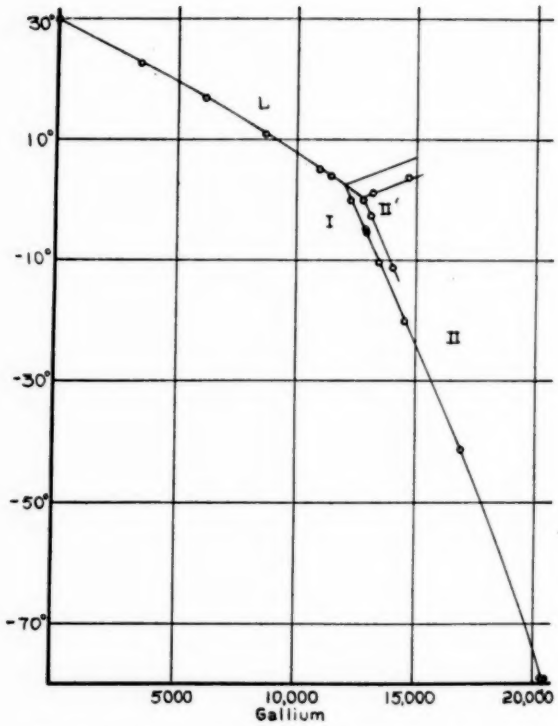

FIG. 9. The phase diagram of gallium, pressure in kg/cm² as abscissa against temperature in degrees Centigrade as ordinate.

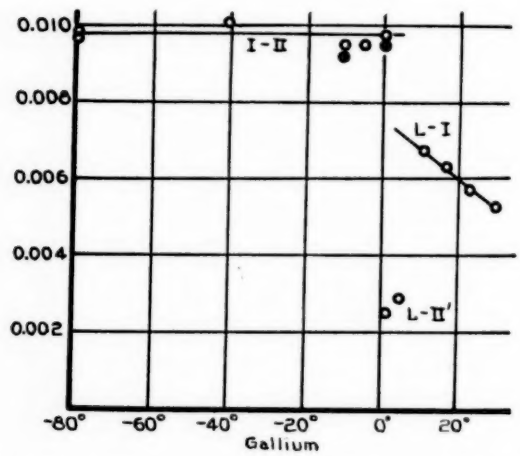

FIG. 10. The volume changes for the transitions of gallium, temperature in degrees Centigrade as abscissa against volume change in cm³/g as ordinate. The filled-in circles are for the transition I–II'.

Iodine

This was found to have a transition at CO_2 temperature with small but unmistakable change of volume. The pressure limits of the transition are unusually wide; the transition runs to completion at once with increasing pressure at 20,600 kg/cm², and on decreasing pressure the transition runs at once to completion on reaching 10,800. The run was repeated with complete check both for the pressure limits and for the volume change, which is between 0.004 and 0.005 cm³/g. A run was then made at 40°, and no perceptible difference was found in the pressure limits or in the change of volume. No other transition was found up to 53,000 at either temperature. A second set-up was then made, and readings made on a time schedule twice as long as on the first set-up, two minutes between readings instead of one, in the endeavor to narrow the pressure range. This was moderately successful, the pressure range now being 6000 instead of 9800, and the mean pressure 12,500 instead of 15,700. The volume change was essentially the same as before. It is therefore probable that the transition line of iodine runs nearly vertically, that is, with small latent heat, at a pressure not far from 13,000, and a volume change not far from 0.0045 cm³/g.

The shearing apparatus gave both on the first trial and on repetition an unmistakable discontinuity with increasing pressure at about 20,000, which is doubtless the transition just described. But a second set-up showed practically nothing with increasing pressure and only a minor break with decreasing pressure. This emphasizes the fact that the shearing measurements give only qualitative indications of transitions.

Summary of Explorations for the Elements Giving Negative Results

There follows now a brief summary of these elements for which negative results were obtained by the volumetric method. It must be again emphasized that the sensitiveness is not as great as is possible at low pressures with the former apparatus, in which the pressure is transmitted by a true liquid. The greatest difficulty arises from friction; this results in irregularity of the readings, the motion of the piston having a tendency to take place in jumps. These jumps simulate small transitions. What is more, sometimes the jumps repeat themselves both with increasing and decreasing pressure. In these cases it is particularly difficult to be sure that small transitions have not been missed. However, I do

not believe that on the average any transition with volume change much larger than 0.001 cm^3/g would have escaped detection.

The arrangement in the following is by columns in the periodic table.

Lithium. Nothing to 46,000 at CO_2 temperature.

Potassium. Nothing to 52,000 at CO_2 temperature.

Caesium. Probably nothing to 52,000 at 0°. This is more doubtful; there is some evidence for a transition at 25,000. Discontinuities were found four times both with increasing and decreasing pressure, but the uncertainty is particularly large here because of the very great compressibility of caesium, and I am inclined to think that the discontinuities were the result of friction.

Gold. Nothing to 51,500 at room temperature. The compressibility of gold stands strikingly out of line with that of copper and silver, and it therefore seemed to me not unlikely that a transition might be found.

Magnesium. Nothing to 51,000 at CO_2 temperature nor to 39,000 at 150°C.

Calcium. Nothing to 51,000 at CO_2 temperature.

Cadmium. This is known to have two new modifications at room temperature with very small volume change.[9] The transitions are very hard to detect, and up to now have been found only with single crystal material; the pressure of the two transitions is nearly the same, and in the neighborhood of 5000. Runs with the new volumetric apparatus were made at CO_2 temperature. It is fairly certain that there was a transition with increasing pressure near 20,000. The same result was found on repetition, but the transition could not be found with decreasing pressure. It is not unlikely that this is the transition already found at room temperature, made highly viscous by the low temperature. If this is the explanation it means that the reverse transition ran so close to atmospheric pressure that it could not be disentangled from the various creep effects always present at the zero on release of pressure. No other transition was found to 44,000 at CO_2 temperature. It would probably pay to examine this metal further at other temperatures.

[9] P. W. Bridgman, Proc. Am. Acad. **60**, 346 (1925).

Barium. Nothing to 51,000 at CO_2 temperature nor +150°.

Indium. Nothing to 50,000 at room temperature. The crystalline structure of indium is tetragonal, rather unusual in a metal; a transition would not have been surprising.

Carbon, graphite. Nothing to 52,000 at CO_2 temperature nor 155°.

Germanium. Nothing to 52,000 at room temperature; the friction was unusually high.

Tin. Probably nothing to 51,000 at CO_2 and room temperature; the shearing experiments suggest a transition.

Lead. Nothing to 52,000 at CO_2 temperature nor at 150°.

Phosphorus, dense variety of black phosphorus. At CO_2 temperature nothing was found to 52,000; the cylinder broke at the maximum. The second set-up gave nothing at 150° to 36,000, where the cylinder broke. In both cases the break was evidently due to chemical attack.

Arsenic. Two independent set-ups were used. The first gave nothing to 50,000 at 140° and the second nothing to 52,000 at 20° and 100°. A transition was expected because of the similarity of the crystal structure to that of bismuth.

Antimony. Nothing was found to 52,000 at room temperature or at 125°. A transition was expected because of the similarity of bismuth and antimony. However, it was found in the shearing experiments that there is very probably a transition near 50,000, which may have been suppressed in these volumetric experiments by viscosity.

Sulfur, amorphous modification. This showed nothing to 40,000 at room temperature, where the cylinder broke, doubtless by chemical attack, since the sulfur was directly in contact with the steel.

Selenium. The amorphous variety was examined at CO_2 temperature to 44,000. There were two rather large jumps during increasing pressure between 25,000 and 30,000 in the direction of increasing density, and one would therefore suspect an irreversible transition to the metallic form. However, a direct determination of the density after the run showed no permanent change. The matter should be examined further.

The metallic form showed nothing to 46,000 at CO_2 temperature nor at +155°.

Other Elements Probably Polymorphic at High Pressure

There is repeated here for the sake of completeness a list of elements which the method of shearing described in a previous paper has shown to be probably polymorphic at high pressure, namely: lithium, calcium, vanadium, manganese, zinc, strontium, yttrium, antimony, barium, lanthanum, cerium, praseodymium, erbium, and thorium.

Some of these elements appear in the list which have given negative results by the volumetric method of this paper. It is probable that in such cases the volume change may be too small to detect. The other elements which have given positive indications by the shearing method have not yet been investigated by the volumetric method.

Results for Compounds

We now pass from the elements to consider a few simple compounds. The systematic investigation of polymorphism among the compounds will evidently be very time consuming; I am planning to take up this investigation in the near future. Most of my activity in this preliminary investigation was confined to the alkali halides. One or another of these salts was investigated a good many times in the course of the development of the apparatus. One would suspect that by the application of sufficient pressure the potassium, sodium, and lithium salts could be made to undergo transition from the simple cubic NaCl structure to the body-centered CsCl structure, since this transition has already been found in the rubidium halides at moderate pressures. The expected transition was found almost at once with the potassium salts at pressures in the neighborhood of 20,000, but apparently pressures higher than 50,000 will be required for the transitions of the sodium and lithium salts.

KCl. Clear single crystal material was used. Measurements have been made on this substance with five different set-ups, and in spite of this the data are not as complete as for the other two potassium halides. Three cylinders ruptured during the measurements; the rupture of one was almost certainly due to the chemical action of the metallic sodium in which the NaCl was embedded in order to make pressure more nearly hydrostatic. The other ruptures I think were probably just bad luck, due to damage received in previous exposures. One cylinder ruptured in which the KCl was protected from contact with the steel with a sheath of lead, and in the other no protection was used. Four of the five set-ups were made with the same type of cylinder as that used for the first measurements with bismuth; the fifth was an early form of the small (6 mm piston) apparatus, from which the stopper shaped cylinder later evolved.

The experimental results are shown in Fig. 11.

KBr. Clear single crystal material was used. Two independent sets of measurements were made, at six temperatures altogether, with the same cylinder, of the double piston bismuth type, with no accident. The results are shown in Fig. 12. The regularity of the results is, I think, surprising, in view of the very great difference between the readings obtained with increasing and decreasing pressure, due both to the friction of the pistons, and the intrinsic width of the region of indifference itself. This latter, judging from comparison with other transitions, must be very much the more important factor at low temperatures. At room temperature there was a difference in the transition pressures of 13,600 kg/cm² when approached from above and below. This decreases irregularly with increasing temperature; at 235° it had dropped to about 3000.

KI. In addition to the first exploratory runs, when the existence of transitions in this series of compounds was first found, runs were made at four temperatures with the double piston bismuth apparatus, and at room temperature with the same early form of the 6 mm piston apparatus as used with KCl. The results are shown in Fig. 13. The pressure difference between increasing and decreasing readings is about the same as for KBr, being 13,400 at room temperature, and dropping off with increasing temperature, but perhaps not as rapidly as for KBr. The great width of the band of indifference explains why the transition was not found before at room temperature in an exploration up to 20,000.[10]

Comparison of the results for the six rubidium

[10] P. W. Bridgman, Zeits. f. Krist. **67**, 371 (1928).

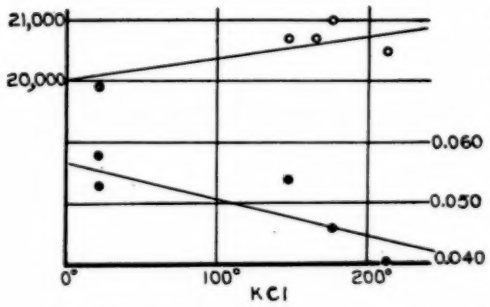

FIG. 11. The transition parameters of KCl. Temperature in degrees Centigrade as abscissa against pressure in kg/cm² as left-hand ordinate, with the corresponding points shown as open circles, and volume change in cm³/g as right-hand ordinate, with the corresponding points as filled-in circles. Notice that the usual order of the pressure-temperature coordinates is here reversed.

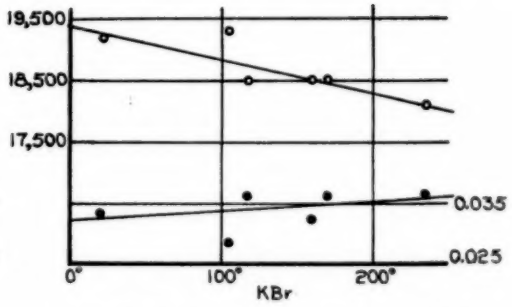

FIG. 12. The transition parameters of KBr. Temperature in degrees Centigrade as abscissa, against pressure in kg/cm² as left-hand ordinate, with the corresponding points shown as open circles, and volume change in cm³/g as right-hand ordinate, with the corresponding points as filled-in circles. Notice that the usual order of the pressure-temperature coordinates is reversed.

and potassium salts shows some interesting resemblances. At temperatures below 200° the order of the transition pressures is the same in the potassium and the rubidium series, the transition pressure increasing from the iodide to bromide to chloride. This is the reverse of the order in the series NH_4Cl, NH_4Br, NH_4I. At 0° the pressure difference between iodide and chloride is not dissimilar in the potassium and rubidium series. Above 200° the transition curves for potassium iodide and bromide cross; in the rubidium series there will probably also be crossing, but at higher temperatures.

The important thermodynamic parameters of the transitions at 130° are collected in Table V.

TABLE V. *Transition parameters of the potassium halides at 130°C.*

Salt	Pressure (kg/cm²)	ΔV (cm³/g)	Fractional Decrease of Volume	$\frac{dT}{dp}$	Latent Heat (kg cm/g)	Latent Heat (g cal./g)	Change of Internal Energy (kg cm/g)
KCl	19,900	0.055	0.108	+0.200	−84	−1.97	+1006
KBr	19,300	.032₅	.102	−0.188	+52	+1.22	680
KI	17,850	.026₅	.087	+0.430	−18	− .42	472

The density of the ordinary modification at the pressure of transition was obtained by extrapolating the second degree formulas which have been found for the compressibility in the range up to 12,000.[11] The corresponding fractional changes of volume at the transition in the rubidium series, from chloride to iodide was: 14.6, 11.3 and 10.7 percent. The order is thus seen to be the same in the rubidium and potassium series. The numerical magnitudes are somewhat less in the potassium series; this is to be expected because of the much higher pressure of the transition.

The latent heats are seen to be only a small part of the total energy change during the transition. The order of energy change is the same in the potassium and rubidium series; the absolute magnitudes are several-fold greater in the potassium series, as is also the range from chloride to iodide.

Other compounds. This covers the compounds the transitions of which have been measured up to the present with the 50,000 apparatus. In

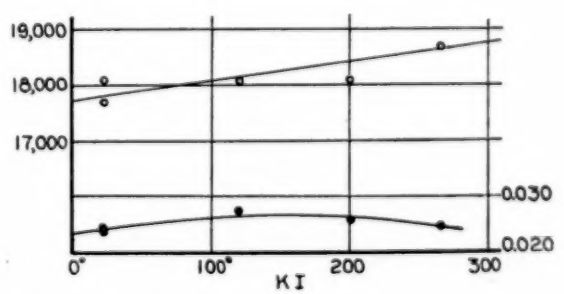

FIG. 13. The transition parameters of KI. Temperature in degrees Centigrade as abscissa, against pressure in kg/cm² as left-hand ordinate, with the corresponding points as open circles, and volume change in cm³/g as right-hand ordinate, with the corresponding points as filled-in circles. Notice that the usual order of the pressure-temperature coordinates is reversed.

[11] J. C. Slater, Proc. Am. Acad. **61**, 135 (1926).

addition, a number of explorations have been made with negative results. Naturally the greatest amount of effort was spent in trying to find the transition in the sodium series. NaCl gave nothing at room temperature with two different set-ups, the first to 32,000 and the second to 50,000. NaI is the member of the series that would be expected to show the transition most readily; this gave negative results at room temperature with four different set-ups, to 46,000, 49,000, 48,000, and 57,000, respectively. However, it has already been mentioned in the previous paper that the shearing curve of NaI begins to bend over at 50,000, and I believe the transition is not far away.

Another interesting salt of the alkali halides series is CsF; this crystallizes with the NaCl structure, although all the other caesium salts are body-centered cubic. One might expect to be able to force the transition to the body-centered structure by high pressure. Two separate set-ups with CsF, for which I am again indebted to Dr. R. W. G. Wyckoff, gave negative results, the first to 42,000 at room temperature, and the second to 56,000 at 137°. It would thus appear that the fluorides are qualitatively different from the other halides. In view of the failure to obtain the transition with CsF, it seemed hardly worth while to explore the fluorides of any of the other alkali metals.

In addition to these, sugar gave negative results to 40,000 at room temperature, and BaS to 39,000 at room temperature. PbTe, on the other hand, probably has a small transition at a mean temperature of 18,000, but this is not certain; there is no further transition up to 39,000. The explorations mentioned in this paragraph were made with a preliminary form of apparatus, only one-third as sensitive as the final form.

I am indebted to the Rumford Fund of the American Academy of Arts and Sciences for financial assistance in purchasing some of the supplies.

DECEMBER 1, 1935 PHYSICAL REVIEW VOLUME 48

Intranuclear Forces

EUGENE FEENBERG* AND JULIAN K. KNIPP, *Research Laboratory of Physics, Harvard University*

(Received August 16, 1935)

Quantitative information as to the nature of intranuclear forces has been obtained by considering the hydrogen and helium isotopes, using a Hamiltonian of the exchange type based on the neutron-proton model with interactions between all the particles. The interactions between like particles are taken to be the same for protons and for neutrons except for the small Coulomb force between protons which accounts for at least half of the difference in the binding energies of He^3 and H^3. It is not inconsistent with existing experimental evidence to assume the range of such forces to be about the same as the range of neutron-proton forces. By making these assumptions and by using simple attractive potentials, it is found that the forces between like particles are given by a potential with depth not greater than 30 mc^2 and with an effective radius of action which must be less than 2.8×10^{-13} cm to be consistent with experimental data for the binding energies. A more accurate determination of the constants based on assuming a close correlation of the three- and four-body problems with "equivalent" two-body problems gives the depth of the proton-neutron potential as 74 mc^2 and of the like-particle potentials as 26 mc^2 and a range of 2.2×10^{-13} cm for the forces. Reasons for believing in the reliability of the "equivalent" two-body method for determining approximate binding energies for three- and four-body problems are discussed. It is shown furthermore that if the exchange operators multiplying the neutron-proton interaction potentials are assumed to be linear combinations of the Majorana and Heisenberg types, it is possible to explain the large scattering of neutrons on protons at low velocities. The proportion of the Heisenberg to the Majorana operator in the linear combination necessary to obtain the correct scattering is about one-fifth. It is then shown that in the three- and four-body problems such an operator can to a good approximation be represented by an equivalent Majorana operator and that because of this fact the results obtained for nuclear energies and for the magnitude and range of the forces (in which Majorana operators were used) remain the same except that the depth of the potential for like particles is increased from 26 to 41 mc^2. The latter value yields a scattering intensity for protons in hydrogen which agrees qualitatively with the experimental results.

* Now at University of Wisconsin.

Section I. Introduction

WE propose to use the binding energies of the hydrogen and helium isotopes to fix the parameters in a simple exchange type nuclear Hamiltonian based on the neutron-proton model with interactions between all pairs of particles. Several authors have found evidence for large interactions between like particles in the odd-even properties of nuclei.[1] In a previous investigation[2] the same problem was studied, but subject to the assumption, which we do not retain, that the interaction between like particles could be treated as a small perturbation in comparison with the neutron-proton interaction.

The Hamiltonian has the form

$$H=-\tfrac{1}{2}\Sigma\Delta_i-\Sigma J(r_{\nu_i\pi_j})P_{\nu_i\pi_j}-\Sigma' K(r_{\nu_i\nu_j})P'_{\nu_i\nu_j}$$
$$-\Sigma' L(r_{\pi_i\pi_j})P'_{\pi_i\pi_j}+(2\pi)^{1/2}/8\Sigma' 1/r_{\pi_i\pi_j} \quad (1)$$

with the units $m_e c^2$ (510,000 ev) for energy and $h/2\pi c(m_e m_\pi)^{1/2}$ (8.97×10^{-13} cm) for length. There exist several possibilities for the exchange operators P and P' depending on the general character of the forces between the nuclear particles. If these forces are first attractive as two particles approach and then strongly repulsive upon closer approach, the exchange operators may be replaced by unity. The inner repulsive regions prevent the collapse of heavy nuclei which would otherwise occur when the forces are of the ordinary (Wigner) type. Because of the mathematical difficulties connected with the correct treatment of the repulsive regions, this model has not yet been adequately investigated.

If the inner repulsive regions are lacking, the burden of keeping the nuclear volume and binding energy proportional to the total number of particles is put on the exchange operators. These may have the form[3]

$$P_{ij}=(1-g)P_{ij}^M+gP_{ij}^H, \quad (2)$$

a linear combination of the Majorana and Heisenberg exchange operators, and[4]

$$P_{ij}'=\tfrac{1}{3}(1+2P_{ij}^M)=-\tfrac{1}{3}\sigma_i\cdot\sigma_j. \quad (3)$$

Because the wave functions for the hydrogen and helium isotopes are symmetrical in the space coordinates of like particles, we may replace P' by unity for our purposes without loss of generality. It is known from the calculations in FI that the effective width and depth of the neutron-proton potential well required to account for the binding energies of the deuteron and the alpha-particle depend only slightly on whether the forces are of the Wigner or of the Majorana type. Thus, if g is small in comparison with unity, it is possible to compare directly the exchange type nuclear model for the hydrogen and helium isotopes with a model based on a Hamiltonian containing only ordinary forces. For this reason a calculation with the exchange model has a certain generality in that it gives at once quantitative information about the alternative model with attractive forces of the Wigner type and also yields a good qualitative picture of the magnitude of the attractive potential wells when these are associated with inner repulsive regions.

Section II. Potentials

To obtain a manageable problem we set $K(r)$ equal to $L(r)$ and suppose that $K(r)$ and $J(r)$ are proportional. The first assumption finds some support in the fact that at least half of the small difference between the binding energies of H^3 and He^3 can be accounted for as resulting from the Coulomb interaction between the protons in He^3. The second assumption is arbitrary, but does not conflict with the experimental evidence as yet available. The definition of the Hamiltonian is completed by the assumption

$$J(r)=A_{\nu\pi}e^{-\alpha r^2}, \quad K(r)=L(r)=A_{\nu\nu}e^{-\alpha r^2}. \quad (4)$$

The experimental energies have the values[5] $E(H^2)\leqq-4.0$, $E(H^3)\leqq-15.8$, $E(He^4)\leqq-54.0$. From the deuteron equation, $H\psi=E\psi$ with

[1] K. Guggenheim, J. de physique **5**, 253 (1934); L. A. Young, Phys. Rev. **47**, 972 (1935); H. Bethe, unpublished lectures.

[2] E. Feenberg, Phys. Rev. **47**, 850 (1935), denoted by FI in text; Phys. Rev. **47**, 857 (1935), denoted by FII in text. For discussion of related problems see L. H. Thomas, Phys. Rev. **47**, 903 (1935) and W. V. Houston, Phys. Rev. **47**, 942 (1935).

[3] P_{ij}^M interchanges the space coordinates i and j in a function to which it is applied; P_{ij}^H interchanges both space and spin coordinates.

[4] In Eq. (3) σ_i represents the Pauli spin operator for the ith particle. The equivalence of the two expressions for P_{ij}' can be deduced from a relation derived by Dirac in his *Quantum Mechanics*, first edition, p. 215, Eq. (35). See also Van Vleck, Phys. Rev. **48**, 367 (1935) for a discussion of the operator P_{ij}'.

[5] Chadwick and Goldhaber, Nature **134**, 237 (1934); Oliphant, Kempton and Rutherford, Proc. Roy. Soc. **A149**, 406 (1935).

TABLE I. $A_{\nu\pi}(\alpha)$ *for* $E(H^2)=-4.0$.

$A_{\nu\pi}/\alpha$	3.45	3.66	3.88	4.11	4.35	4.60	4.85
$1/\alpha^{1/2}$	0.12	0.15	0.18	0.21	0.24	0.27	0.30
$A_{\nu\pi}/\alpha$	5.10	5.36	5.71	6.16	6.65	7.17	7.70
$1/\alpha^{1/2}$	0.33	0.36	0.40	0.45	0.50	0.55	0.60

$E=-4.0$, $A_{\nu\pi}$ is obtained as a function of α by means of a series of numerical integrations: Table I makes possible the ready determination of the lowest eigenvalue of any two-particle Schrödinger equation with an arbitrary error function type of potential[6] and will be used for that purpose in Section IV. The function $A_{\nu\pi}(\alpha)$ does not depend on the value assigned to g. This is true because the wave function ψ for the deuteron is symmetrical in both the space and spin coordinates of the two particles and hence in this case

$$\{(1-g)P^M+gP^H\}\psi=\psi. \tag{5}$$

When, however, the spins of unlike particles are not completely parallel, the properties of the model do depend on g. In Sections III and IV the discussion is based on the simplifying assumption that the forces between unlike particles are of the pure Majorana type ($g=0$). The general case in which g differs from zero is considered in Section V.

SECTION III. THE SIMPLE VARIATIONAL METHOD

With the Gaussian type of wave function

$$\varphi_0(1;2,3)=Ne^{-(\nu/2)(r_{12}^2+r_{13}^2)-(\mu/2)r_{23}^2},\ (H^3),\ (6)$$

$$\varphi_0(1,2;3,4)$$
$$=Ne^{-(\nu/2)(r_{13}^2+r_{14}^2+r_{23}^2+r_{24}^2)-(\mu/2)(r_{12}^2+r_{34}^2)},\ (He^4),\ (7)$$

the average value of the Hamiltonian operator (omitting the Coulomb terms and setting $g=0$) can be written

$$E^0(H^3)=(2+p)\alpha\sigma-2A_{\nu\pi}\{p(4-p)/(1+2p)\}^{3/2}$$
$$\times(\sigma/(\sigma+1))^{3/2}-A_\nu(p\sigma/(p\sigma+1))^{3/2} \tag{8}$$

for the three-body problem and

$$E^0(He^4)=(3/2)(2+p)\alpha\sigma-4A_{\nu\pi}(2p-p^2)^{3/2}$$
$$\times(\sigma/(\sigma+1))^{3/2}-2A_\nu(p\sigma/(p\sigma+1))^{3/2} \tag{9}$$

for the alpha-particle. These differ from the corresponding expressions in FI (Eqs. (18) and (19)) in the presence of the term proportional to A_ν and in a more suitable choice of the variation parameters.[7] The contribution from the Coulomb interaction to the energy has the form

$$\Delta E=\tfrac{1}{4}(2\alpha p\sigma)^{1/2} \tag{10}$$

for both He^3 and He^4. The values of p and σ which minimize (8) and (9) must be found by trial. However the dependence on p is slight, the best value generally being between 0.9 and 1.0.

Let $A_\nu(\alpha, H^3)$ and $A_\nu(\alpha, He^4)$ represent the functions defined by the conditions that the accurate lowest eigenvalues of the three- and four-body problems have the experimental values $E(H^3)=-15.8$ and $E(He^4)=-54.0$, respectively. Eqs. (8) and (9) can be used to obtain upper bounds on $A_\nu(\alpha, H^3)$ and $A_\nu(\alpha, He^4)$. Consider first Eq. (9). There exists a function $A_\nu^0(\alpha, He^4)$ such that if A_ν is replaced by $A_\nu^0(\alpha, He^4)$ in (9) the minimum value of $E^0(He^4)+\Delta E$ with respect to p and σ coincides with the experimental energy. By the minimum property of the variation method, we have

$$A_\nu(\alpha, He^4)\leqq A_\nu^0(\alpha, He^4). \tag{11}$$

We find that $A_\nu^0(\alpha, He^4)$ is practically constant with the value 30 mc^2 on the range $10\leqq\alpha\leqq50$. In the same way we find that $A_\nu^0(\alpha, H^3)$ varies from the value 30 mc^2 at $\alpha=10$ to 100 mc^2 at $\alpha=50$. Furthermore the difference $A_\nu^0(\alpha, H^3)-A_\nu(\alpha, H^3)$ is much greater than the corresponding difference $A_\nu^0(\alpha, He^4)-A_\nu(\alpha, He^4)$. This can be seen from the fact that the binding energy in the three-body problem is a small difference between large potential and kinetic energy terms. Hence the energy is sensitive to errors in the wave function. The same statement is true for the alpha-particle, but in a much less extreme degree. Thus the correct value of A_ν is less than 30 mc^2 and the correct value of α is greater than 10 ($1/\alpha^{1/2}<2.8\times10^{-13}$ cm).

SECTION IV. THE "EQUIVALENT" TWO-BODY METHOD

To improve upon these inequalities we have recourse to the method of the "equivalent" two-

[6] FI, Eq. (4).

[7] In Eq. (8) $4\alpha\sigma=5\nu+\mu$, $2\alpha\sigma p=\nu+2\mu$; in Eq. (9) $2\alpha\sigma=3\nu+\mu$, $\alpha\sigma p=\nu+\mu$.

body problem described and used in FI. The method is not rigorous, but its general correctness is supported by the considerations advanced in FI and by the results of attempts to improve on Eqs. (8) and (9) with more complicated variational calculations (see appendix). The procedure involves first replacing p by unity in both (8) and (9) in order to reduce the two different potential energy terms to the same form. In FI because there was only one kind of potential energy term, this simplification was unnecessary. The resulting simplified expressions have exactly the form taken by the corresponding expression for the variational problem associated with the equation

$$\{d^2/dr^2+E'+Be^{-\beta r^2}\}\varphi=0 \qquad (12)$$

when the approximate wave function $\varphi=e^{-\nu r^2/2}$ is used to evaluate the energy integral. The formal analogy is made exact by the identifications

$$\left.\begin{aligned}\beta&=2\alpha\\ B&=2A_{rr}+A_r\end{aligned}\right\}\mathrm{H}^3,\qquad \left.\begin{aligned}\beta&=3\alpha\\ B&=2(2A_{rr}+A_r)\end{aligned}\right\}\mathrm{He}^4. \qquad (13)$$

These identifications establish a correspondence between the three and four-body problems and "equivalent" two-body problems which can be solved accurately. To proceed further we insert into (12) the experimental value for E' and, using Table I, compute B and hence A_r as a function of α for both H^3 and the alpha-particle. We designate these functions by the symbols $A_r'(\alpha, H^3)$ and $A'(\alpha, He^4)$. Small corrections to make up for the inaccuracy resulting from setting $p=1$ are easily determined by means of Eqs. (8) and (9). Results are exhibited in Tables II and III. Table II includes a column giving the binding energy of H^3 as a function of α when $A_r(\alpha)=A_r'(\alpha, He^4)$. At the point of intersection $(A_r'(\alpha, H^3)=A_r'(\alpha, He^4))$ α has the value 17 $(1/\alpha^{1/2}=2.17\times10^{-13}$ cm), $A_{rr}=74.3\ mc^2$ and $A_r=26\ mc^2$. The figures given by Young[1] can be compared with the $\alpha=10$ column in Table II by noting that $\frac{1}{3}(2A_{rr}+A_r)$ corresponds to the depth of the rectangular potential function used in Young's calculation. There is satisfactory qualitative agreement.

All the results of this and the preceding sections can be extended without difficulty to other forms of the attractive potentials, in particular, to the rectangular potential well and the straight exponential function. The interesting generalization of taking different radii of action for the forces between like and between unlike particles can also be treated by the same methods, but would involve a large amount of numerical computation.

TABLE II. *The "equivalent" two-body method for the determination of $A_r'(\alpha, He^4)$.*

α	A_{rr}	A_r'	$-E'(He^4)$	C.E.(He^4)*	$-E'(H^3)$
10	49.7	29	55.4	1.4	
20	84.4	24	55.6	1.6	15.2
30	117.1	19	55.8	1.8	13.7
40	148.8	12	56.0	2.0	12.8

TABLE III. *The "equivalent" two-body method for the determination of $A'(\alpha, H^3)$.*

α	A_{rr}	A_r'	$-E'(H^3)$	C.E.(He^3)*
10	49.7	22	15.8	1.2
20	84.4	27	15.8	1.4
30	117.1	31	15.8	1.5
40	148.8	33	15.8	1.7

* C. E. in Tables II and III—Coulomb energy.

SECTION V. THE MIXED EXCHANGE OPERATOR

The experimental cross section for the elastic scattering of slow neutrons in hydrogen has about the value[8] 30×10^{-24} cm², which exceeds by a factor of eight the theoretical cross section[9] computed from the neutron-proton potential determined in the preceding section. One of the writers has attempted to explain this descrepency by supposing that the potential depends on the state of the system and on the velocity of the colliding particles in such a way that the interaction potential for scattering is smaller than for binding and decreases with increasing relative velocity.[10] This hypothesis, if correct, should apply equally well to the interaction of two protons. Thus we should expect the anomalous proton-proton interaction potential required to explain the anomalous scattering of protons in hydrogen[11] to be smaller than $K(r)$. In fact $K(r)$ is very much too small to explain White's results.[12] Thus the

[8] Dunning, Pegram, Fink and Mitchell, Phys. Rev. **47**, 970 (1935); Bjerge and Westcott, Proc. Roy. Soc. **A150**, 790 (1935).
[9] FII, Eq. (5).
[10] FII.
[11] M. G. White, Phys. Rev. **47**, 573 (1935).
[12] R. D. Present, to be submitted to the Physical Review.

hypothesis advanced in FII must be abandoned.

Wigner[13] has suggested that the very large experimental neutron-proton scattering cross section indicates a dependence of the interaction potential on spin orientation. Eq. (2) represents the mathematical formulation of Wigner's suggestion.[14] In the scattering problem based on the exchange operator of Eq. (2), there occur four distinct wave functions:

$$\psi_1(12)=\varphi(r_{12})\delta(m_1,\tfrac{1}{2})\delta(m_2,\tfrac{1}{2}), \tag{14}$$

$$\psi_2(12)=\varphi_a(r_{12})\delta(m_1,\tfrac{1}{2})\delta(m_2,-\tfrac{1}{2}) + \varphi_b(r_{12})\delta(m_1,-\tfrac{1}{2})\delta(m_2,\tfrac{1}{2}), \tag{15}$$

and two additional functions obtained by reversing the directions of the spin coordinates in ψ_1 and ψ_2. It is readily found that φ and $\varphi_a+\varphi_b$ are solutions of the equation

$$\{\nabla_{12}^2+W+J(r_{12})P_{12}^M\}\psi(r_{12})=0, \tag{16}$$

while $\varphi_a-\varphi_b$ satisfies the equation

$$\{\nabla_{12}^2+W+(1-2g)J(r_{12})P_{12}^M\}\psi(r_{12})=0. \tag{17}$$

An appropriate set of boundary conditions is provided by the following statement: the functions φ and φ_a have the form of an incident plane wave plus a scattered wave: the incident wave does not occur in φ_b which contains only a scattered wave. The scattering intensity obtained from ψ_2 is simply the sum of the intensities associated with φ_a and φ_b because there is no interference between scattered waves associated with orthogonal spin wave functions. From this fact can be deduced that the statistical weights of the scattering intensities obtained from the potential fields $J(r)$ and $(1-2g)(Jr)$ are in the ratio three to one. The scattering cross section for slow neutrons can be made as large as desired by choosing g to bring the lowest eigenvalue of Eq. (17) sufficiently near the top of the potential hole, or, equally well, by taking g so large that Eq. (17) just fails to have a discrete state. For the effective radius determined in the preceding section these conditions are met with $g\sim 0.2$.

The effect of the mixed operator on the three- and four-body problems may be studied most simply when g is small by means of a first order perturbation calculation. When g vanishes, the alpha-particle wave function can be written in the form

$$\psi(1,2;3,4)=\varphi(x_1,x_2;x_3,x_4) \times S(m_1,m_2)S(m_3,m_4) \tag{18}$$

with

$$S(m_1,m_2)=1/2^{1/2}\{\delta(m_1,\tfrac{1}{2})\delta(m_2,-\tfrac{1}{2}) -\delta(m_2,\tfrac{1}{2})\delta(m_1,-\tfrac{1}{2})\}. \tag{19}$$

The average value of the mixed neutron-proton potential is simply

$$4\sum_{\text{Spin}}\int\cdots\int\psi(1,2;3,4) \times\{(1-g)P_{13}^M+gP_{13}^H\}\psi(1,2;3,4)d\tau, \tag{20}$$

which reduces to

$$4(1-g/2)\int\cdots\int\varphi(x_1,x_2;x_3,x_4) \times J(r_{13})P_{13}^M\varphi(x_1,x_2;x_3,x_4)d\tau \tag{21}$$

when the summation over the spin coordinates is carried out. Thus in this problem for small values of g the mixed operator can be replaced by an "equivalent" pure Majorana operator:

$$(1-g)P^M+gP^H\rightarrow(1-g/2)P^M. \tag{22}$$

The same result is obtained from the analogous treatment of the three-body problem.

It is clear from Eq. (13) that the calculations in Section IV determine essentially the quantity $2A_{\nu\pi}+A_\nu$ and not A_ν directly. Consequently

$$2A_{\nu\pi}+A_\nu\sim(2-g)A_{\nu\pi}+\bar{A}_\nu, \tag{23}$$

and

$$\bar{A}_\nu\sim A_\nu+gA_{\nu\pi} \tag{24}$$

if $\bar{A}_\nu$ is written for the amplitude of the interaction between like particles when g differs from zero. With $1/\alpha^{1/2}\sim 2.2\times10^{-13}$ cm, $A_\nu\sim 26$, $A_{\nu\pi}\sim 74$ and $g\sim 0.2$, we get

$$\bar{A}_\nu\sim 41mc^2. \tag{25}$$

Present[12] has computed the anomalous scattering of protons in hydrogen to be expected from

[13] Unpublished; mentioned by Professor Bethe at the Washington Conference on Nuclear Physics.

[14] Van Vleck, Phys. Rev. **48**, 367 (1935), note 20.

the potential defined by Eq. (25) and finds rough qualitative agreement with White's measurements.[11] To summarize: Wigner's suggestion that the neutron-proton interaction potential depend on spin orientation does not appreciably change the binding energy problem, but does enable us to understand the remarkable experimental results on the scattering of slow neutrons and fast protons in hydrogen. It should be mentioned that the theoretical cross section for elastic scattering of fast neutrons in hydrogen is somewhat larger than the rather uncertain experimental value.

Appendix

Comparison of Improved Variational Calculations for Two- and Three-Body Problems

Further justification for the use of the method of the "equivalent" two-body problem for calculating energies for three-body problems is obtained when the results of attempts to improve the variational calculations in the two problems are compared. The "equivalent" two-body problem is determined in both the Wigner and Majorana cases by identifying certain constants in the expressions for the energy obtained when simple Gaussian-type wave functions are used. This identification is possible because the energy expressions in this "zeroth" approximation have the same form.

We have used three different methods for improving the variational calculations beyond the zeroth stage. In the first method the original Gaussian functions are multiplied by polynomials in the various distances. For the two-body problem we then have for the wave function (taking only quadratic terms)

$$\varphi(r)=e^{-(\nu r^2/2)}\{a_0+a_1\nu r^2\}. \tag{26}$$

A similar wave function for the three-body problem is given by the expression

$$\varphi(1,2,3)=e^{-(\nu/2)(r_{12}^2+r_{13}^2)-(\mu/2)r_{23}^2}\{C_0+C_1\nu(r_{12}^2+r_{13}^2)+C_2\nu r_{23}^2\}. \tag{27}$$

The calculations were made by using the Majorana operator for the three-body problem (H^3) including the neutron-neutron attraction term. The parameter ϕ was set equal to unity in order to simplify the calculation of the matrix elements. With a given β, B was determined to give $E'=-16$ for the exact eigenvalue of the "equivalent" problem. The corresponding values of $A_{\nu\pi}$, A_ν, α for the three-body problem are taken from Eq. (13). In the three-body problem, the inclusion of the quadratic terms gives an improvement in the energy of only a small fraction of an mc^2 unit over the value obtained with the simple Gaussian function. The fact that the more flexible three-parameter function is no better than the two-parameter Gaussian function simply means that the quadratic terms serve only to correct ν and μ. When these parameters are both varied, the quadratic terms lose their importance. Correspondingly, for the "equivalent" two-body problem, the quadratic term gives no appreciable improvement. This result is of value because it brings out the closeness of the correlation between the three-particle problem and the associated "equivalent" problem.

In general, computations with Majorana interaction terms in the Hamiltonian are more involved than those with the ordinary Wigner type of potential. Moreover, as we show in the next paragraph, there is a Wigner problem closely related to every Majorana problem. For the purpose of showing the close correlation of three-body problems to their "equivalent" two-body problems it is just as instructive and very much simpler to use Wigner interaction potentials.

Let us consider the following closely related three-body problems. Call problem (a) a problem in which we have only neutron-proton potential terms of the Wigner type in the Hamiltonian:

$$-Ae^{-\alpha r_{12}^2}-Ae^{-\alpha r_{13}^2}. \tag{28}$$

In problem (b) take only neutron-proton potential terms of the Majorana type:

$$-Ae^{-\alpha r_{12}^2}P_{12}^M-Ae^{-\alpha r_{13}^2}P_{13}^M. \tag{29}$$

Let problem (c) be the same as (b) except for the addition of a neutron-neutron potential term to the Hamiltonian:

$$-(A-C)e^{-\alpha r_{12}^2}P_{12}^M-(A-C)e^{-\alpha r_{13}^2}P_{13}^M-2Ce^{-\alpha r_{23}^2}. \tag{30}$$

The close relation between problems (a) and (b) was shown in F1; (a) gives slightly lower energies than (b). On the other hand, problems (b) and (c) are both associated with the same "equivalent" two-body problem provided the parameter ϕ is set equal to unity since then for both $B=2A$. Problem (c) gives slightly lower energies than problem (b) since in passing from the "equivalent" problem for (c) to that for (b) the parameter ϕ is fixed at unity. We thus see that problem (a) and problem (c) are very closely related. For the rest of the discussion we shall use the simple Wigner-type Hamiltonian of problem (a) since the results so obtained are quite general and because to do so greatly simplifies the computations.

We sought to improve the variational calculations by using wave functions which are the sum of functions of the Gaussian type but with different ν's and μ's. If we take

$$\psi=\psi_\sigma+\lambda\psi_{\sigma'}, \tag{31}$$

then appropriate wave functions for the two-body problem are obtained by substituting for ψ_σ

$$\psi_\sigma=Ne^{-(\nu r^2/2)},\qquad \nu=\beta\sigma, \tag{32}$$

and for $\psi_{\sigma'}$ a similar expression having $\nu'=\beta\sigma'$. The matrix elements then are

$$(\sigma/1/\sigma')_2=\{4\sigma\sigma'/(\sigma+\sigma')^2\}^{3/4}\equiv\gamma,$$
$$(\sigma/\mathrm{H}/\sigma')_2=\gamma\{3\beta\sigma\sigma'/(\sigma+\sigma')-B((\sigma+\sigma')/(\sigma+\sigma'+2))^{3/2}\}. \tag{33}$$

In our wave function for the three-body problem we use for $\psi\sigma$ the function given by Eq. (6), with $\nu=\alpha\sigma(1+n)/(1+2n)$ $n=\mu/\nu$, and for $\psi\sigma'$ a similar expression. The matrix elements are simplified if we specialize the function by taking $n'=\mu'/\nu'=n$, thus reducing the number of parameters by one. This simplification makes it possible to put the matrix elements in the same form as those of the two-body problem. In fact we have

$$(\sigma/1/\sigma')_3=\{4\sigma\sigma'/(\sigma+\sigma')^2\}^{3/2}=\gamma^2,$$
$$(\sigma/\mathrm{H}/\sigma')_3=\gamma^2\left\{3\alpha\frac{2+3n+n^2}{1+2n}\frac{\sigma\sigma'}{\sigma+\sigma'}-2A\left(\frac{\sigma+\sigma'}{\sigma+\sigma'+2}\right)^{3/2}\right\}. \tag{34}$$

The value of n which minimizes the zeroth approximation $(\sigma/\mathrm{H}/\sigma)_3$ to the three-body energy is very nearly $\frac{1}{3}$, independent of A, α and σ. As in the case of the polynomial method, B and β are determined so that E' for the two-body problem has the value -16. A and α are such as to establish an "equivalence" between the two problems in the zeroth order and are given by the relations

$$\beta=(28/15)\alpha, \qquad B=2A. \tag{35}$$

Although A is the amplitude of the neutron-proton interaction, it is not directly connected with the $A_{\nu\pi}$ considered in Section IV since here we have a Wigner Hamiltonian and no interaction between like particles. In this problem A plays the same role as $A_{\nu\pi}+\frac{1}{2}A_\nu$ in the actual problem. Taking the same value of σ and n throughout (σ, best value for the zeroth approximation, $n=\frac{1}{3}$) and varying σ' we obtain about 19 and 17 percent improvement in the two- and three-body problems, respectively. If σ, σ' and n are all varied the improvement is 51 percent in the three-body problem and 86 percent in the two-body problem. A part of this difference must result from the assumption $n'=n$ which restricts considerably the flexibility of the three-body function. Moreover the three-body wave function contains only even powers of the distances r_{12}, r_{13}, r_{23} and hence lacks an essential part of the true solution. For these two reasons it is thought that the difference in the improvements found in the two problems is without significance.

The Hassé method[15] was the third method used to improve the wave functions and the one which gave the greatest improvement in the case of the three-body problem. The Hassé method has the great advantage that it automatically introduces into the wave function essential terms which may be lacking in the zeroth approximation. Suppose that in either problem H is the Hamiltonian and ψ_0 is the Gaussian wave function; we take as our new wave function

$$\psi=(1+\lambda H)\psi_0, \tag{36}$$

where λ is a parameter to be varied. In the two-body problem ψ is a two-parameter function while in the three-body problem it is a three-parameter function.

The matrix elements of H, H^2, H^3 and unity are necessary to the calculation. For the "equivalent" problem they are (with $B=2A$, $\beta=(28/15)\alpha$)

$$\begin{aligned}
&(0/1/0)=1,\\
&(0/\mathrm{H}/0)=2.8\alpha\sigma-2A(\sigma/(\sigma+1))^{3/2},\\
&(0/\mathrm{H}^2/0)=13.07(\alpha\sigma)^2-0.4\alpha A(\sigma/(\sigma+1))^{5/2}(28\sigma+56)\\
&\qquad+4A^2(\sigma/(\sigma+2))^{3/2},\\
&(0/\mathrm{H}^3/0)=85.37(\alpha\sigma)^3-5.23\alpha^2A(\sigma/(\sigma+1))^{7/2}\\
&\qquad\times(15\sigma^2+52\sigma+52)\\
&\qquad+11.2\alpha A^2(\sigma/(\sigma+2))^{5/2}(3\sigma+12+4/\sigma)\\
&\qquad-8A^3(\sigma/(\sigma+3))^{3/2}.
\end{aligned} \tag{37}$$

The matrix elements of unity and H are given correctly by Eq. (37) for both problems. Those of H^2 and H^3 in the three-particle problem are (with $n=\frac{1}{3}$)

$$\begin{aligned}
&(0/\mathrm{H}^2/0)=10.67(\alpha\sigma)^2-0.4\alpha A(\sigma/(\sigma+1))^{5/2}(28\sigma+43)\\
&\qquad+2A^2[(\sigma/(\sigma+2))^{3/2}+(\sigma^2/(\sigma^2+2\sigma+15/16))^{3/2}],\\
&(0/\mathrm{H}^3/0)=51.77(\alpha\sigma)^3-\alpha^2A(\sigma/(\sigma+1))^{7/2}\\
&\qquad\times(64\sigma^2+184.8\sigma+143.3)\\
&+0.2\alpha A^2[(\sigma^2/(\sigma^2+2\sigma+15/16))^{5/2}(84\sigma+258+165/\sigma)\\
&\qquad+(\sigma/(\sigma+2))^{5/2}(84\sigma+258+60/\sigma)]\\
&\qquad-2A^3[(\sigma/(\sigma+3))^{3/2}+3(\sigma^2/(\sigma^2+3\sigma+15/8))^{3/2}].
\end{aligned} \tag{38}$$

We find about 65 percent improvement in the energy for the two-body problem with this method and about 60 percent improvement for the three-body problem. It is interesting to note that the matrix elements have somewhat the same form in the two problems except for different numerical factors and certain correction terms. The numerical values of the matrix elements $(0/\mathrm{H}^2/0)$ and $(0/\mathrm{H}^3/0)$ are quite different in the two problems because of these differences. The fact that the corrections obtained are a few percent smaller for the three-body problem than for the two-body problem is thought to be of no significance because one of the parameters which appear in the three-body problem was fixed at a probable value and not varied further.

These investigations establish the inequality

$$E(\mathrm{H}^3)<E^0(\mathrm{H}^3)+0.6\{E'(\mathrm{H}^3)-E^0(\mathrm{H}^3)\} \tag{39}$$

and lend strong support to the view that $E(\mathrm{H}^3)$ does not differ very much from $E'(\mathrm{H}^3)$.

This paper was begun at Harvard and completed at the summer session of the University of Michigan. We wish to express our appreciation of the courtesy and hospitality shown by the Michigan Physics Department.

[15] H. R. Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930).

Note on the Interaction of Nuclear Particles

LLOYD A. YOUNG, *Research Laboratory of Molecular Physics, Carnegie Institute of Technology*

(Received August 29, 1935)

Simple approximate calculations of the ranges and strengths of the interactions of nuclear particles lead to the following conclusions: The interactions are of an exchange nature with the range approximately 2.8×10^{-13} cm. The neutron-neutron and proton-proton interactions are approximately equal. The neutron-proton interaction probably depends upon spin orientation. For parallel spins the order of magnitude of the interaction is 40 mc^2, for antiparallel spins 25 mc^2. It is further concluded that a di-neutron or di-proton may be dynamically stable, but unstable with respect to β-decay.

IN a recent publication,[1] the writer gave arguments for the existence of neutron-neutron and proton-proton (to be denoted hereafter as $\nu-\nu$ and $\pi-\pi$) exchange interactions comparable in range and strength with the $\nu-\pi$ interactions. It was found that the empirical data on binding energies of heavy nuclei could be explained fairly well by taking all these possible interactions of the same range and strength. In terms of a potential "hole" the range was found to be just $\epsilon^2/mc^2=2.8\times10^{-13}$ cm, and the strength 40 mc^2. It is the purpose of the present note to give very simple approximate calculations of these quantities and to indicate how the assumption of equal interactions needs to be modified.

A. Range of Interactions

From experimental data on nuclear radii we can obtain considerable information as to the range of the interactions among the nuclear particles. For if, as is certainly the case, the interactions are of an exchange nature the forces holding α-particles and paired-neutron groups together will depend on wave function overlapping in much the same manner as valence binding in molecules. In such molecules the interatomic distances are related simply to the radii of the atoms concerned ($d_{ij}\sim r_i+r_j$). Thus in a nucleus we should expect each α-group and ν^2-group to occupy its own volume, so that the nuclear volume, V, is of the order AV_0. This is in agreement with experiment.[2] Further, V_0 cannot be far from the volume of the sphere of action of the $\nu-\pi$, $\nu-\nu$, and $\pi-\pi$ exchange forces. This means that we can use experimentally determined nuclear sizes to get at the radius of action of these forces.

The lead nucleus has a cross section for the scattering of fast neutrons[3] $\sigma=5.7\times10^{-24}$ cm^2, corresponding to a collision radius of 1.35×10^{-12} cm. This collision radius we may expect to be of the order $R_\nu+r$, where R_ν is the nuclear radius measured to the outermost layer of ν^2-groups and r is the radius of action of the exchange forces. There are 60 groups of paired neutrons in the Pb nucleus, so $R_\nu\sim(60)^{\frac{1}{3}}r$, whence

$$r\sim2.7\times10^{-13}\text{ cm}.$$

Similarly the radius of the same nucleus extrapolated from α-decay data is $\sim7.8\times10^{-13}$ cm. This radius probably measures the distance from the center of the nucleus to somewhere within the outermost layer of α-particles, i.e., 7.8×10^{-13} cm $\sim R_\alpha-\frac{1}{2}r$. There are 40 α-particles in this nucleus, so $R_\alpha\sim(40)^{\frac{1}{3}}r$, whence $r\sim2.6\times10^{-13}$ cm. The agreement of these two values for r does not mean that either is very accurate. Actually by such calculations we can only say that r lies between 2.4×10^{-13} cm and 3.0×10^{-13} cm. The fact that nuclear radii from neutron scattering are, in general, larger than radii from α-decay data makes it seem reasonable to believe that *extra* neutrons in nuclei are in ν^2-groups which form something of the nature of a "monomolecular" layer over the core of the nucleus which is made up of α-particles.

[1] L. A. Young, Phys. Rev. **47**, 972 (1935). In this paper a factor $\frac{1}{2}$ is omitted in the proposed nuclear potential energy.

[2] For this reason we give below numerical calculations of range of interactions for only one nucleus. Any other nucleus could have been used.

[3] J. R. Dunning, G. B. Pegram, G. A. Fink and D. P. Mitchell, Phys. Rev. **48**, 265 (1935).

B. Order of Magnitude of $\nu-\nu$ Interaction

The more accurate knowledge of atomic weights (particularly of the lightest elements) given by transmutation data[4] makes it possible to gain some idea of the neutron-neutron interaction in a very direct way. Bethe gives

$$C_{13}-C_{12}=1.0032; \qquad O_{17}-O_{16}=1.0040.$$

These differences correspond to the addition of a single neutron to a nucleus made up of α-particles. Subtracting these from the neutron mass gives the binding energy between the unpaired neutron and the rest of the nucleus. From the above this binding energy is $\sim 8\ mc^2$.[5] If we now take mass differences for nuclei which differ by one ν^2-group we can hope to get at the $\nu-\nu$ interaction. Unfortunately, Bethe did not have such data to include in his study of masses. Determinations have been made with the mass spectrograph, however, and yield for $Ne_{22}-Ne_{20}$ and $Cl_{37}-Cl_{35}$ the value 1.9980. This corresponds to a mass decrease of 36 mc^2 from the mass of two free neutrons. Of this $\sim 16\ mc^2$ can be accounted for as due to the binding of the two neutrons to the core of the nucleus and 20 mc^2 remains to be attributed to $\nu-\nu$ binding within the ν^2-group itself. This *does not mean* that the free di-neutron is stable with a binding energy $\sim 20\ mc^2$. It is probably just stable. Such a great difference between the binding energy of a free di-neutron and a ν^2-group in a nucleus can be understood if one remembers that the motion of the two particles in a free di-neutron would be of a very constrained type (the center of gravity must remain at rest or move uniformly) with a reduced mass, $\frac{1}{2}M$. Assuming that the radius of interaction for the $\nu-\nu$ forces is just ϵ^2/mc^2 the energy quantization condition for a free di-neutron is

$$\tan\,(0.312[v-w]^{\frac{1}{2}})=-[v/w-1]^{\frac{1}{2}}$$

where v is the depth of the potential hole and w the binding energy, both in units mc^2. The effect of binding the di-neutron to a nucleus would be to increase the effective reduced mass from $\frac{1}{2}M$ to practically M, so that the quantization condition would become

$$\tan\,(0.312[2(v-w)]^{\frac{1}{2}})=-[v/w-1]^{\frac{1}{2}}.$$

If, in this equation we give w the value 20, we can solve for v. We find $v\sim 45$. Thus, if the $\nu-\nu$ interaction be represented by a potential hole of radius ϵ^2/mc^2 the depth is of the order 45 mc^2. Since ν^2-groups have zero spin this is the $\nu-\nu$ interaction for antiparallel spins. Since such paired spins are the usual thing it is hard to find a way to determine how two neutrons (or protons) interact when their spins are parallel. The above calculation is quite rough, but in the next section we give a comparison of the $\nu-\nu$ and $\nu-\pi$ interactions which should be fairly reliable.

C. Comparison of $\nu-\nu$ and $\nu-\pi$ Interactions

The nuclei Li_6, B_{10}, and N_{14} consist of one $(\nu\pi)$-group outside of α-groups. The next nucleus of this sequence, F_{18} does not exist, but O_{18}, having a ν^2-group, is stable. This may be considered as evidence that the $\nu-\pi$ interaction is slightly smaller than the $\nu-\pi$ interaction, although ν^2-groups finally become more stable due to Coulomb interactions. The Coulomb interaction of the proton of the $(\nu\pi)$-group in F_{18} may be estimated to be $\sim 6\ mc^2$ and this means that the effective internal binding of the $(\nu\pi)$-group is $\sim 7\ mc^2$ greater than that of the ν^2-group. This will be reflected in terms of the interactions, so that we may say that the $\nu-\nu$ potential hole is about 7 mc^2 shallower than the $\nu-\pi$ potential.

D. The Filled Potential Hole

The periodic system of elements ends with the natural radioactive families which are unstable with respect to α and β-decay. If we visualize such a nucleus in terms of neutrons and protons moving in a spherical potential hole, then this instability is due to the fact that the energy levels of this hole are filled up to a point so near the top that such transformations are energetically possible. Up to the present, evidence points to the fact that the effective potential for neutrons and protons differs only by the Coulomb

[4] H. Bethe, Phys. Rev. **47**, 633 (1935).

[5] This is the average of two values which differ by almost 20 percent; so from these data alone one cannot say that the binding of a single neutron is independent of the number of α-particles in the nucleus. Mass differences for heavier nuclei, however, give considerable weight to the belief that this is approximately true.

interactions which affect the latter. Thus, if the effective depth of the neutron potential is Φ, the effective depth for a proton is $\Phi-I$ where I is the average Coulomb energy of a proton within the nucleus. This is given by $I\sim(1/2)Z\epsilon^2/R$, where R is the radius of the nucleus or of the potential hole. Now according to the Thomas-Fermi theory, the number, N, of particles occupying states with momenta between 0 and P is given by

$$N=\frac{8\pi V}{h^3}\int_0^P p^2dp=\frac{8\pi V}{3}\left(\frac{P}{h}\right)^3.$$

Since we are going to consider the potential hole for the heaviest nucleus, we write

$$Z_{\max}=(8\pi V/3)(P_\pi/h)^3,$$
$$(A-Z)_{\max}=(8\pi V/3)(P_\nu/h)^3$$

with

$$P_\pi=[2M(\Phi-Z\epsilon^2/2R)]^{\frac{1}{2}} \quad \text{and} \quad P_\nu=(2M\Phi)^{\frac{1}{2}}.$$

The uranium nucleus is the heaviest, so if we substitute 92 for $Z_{\max}$ and 146 for $(A-Z)_{\max}$ we have two equations to solve for Φ and V (or R). The solution is

$$R\sim 8.1\times10^{-13}\text{ cm}; \qquad \Phi\sim 140\ mc^2.$$

It is indeed satisfactory that such a simple approximate calculation gives such reasonable results. It should be emphasized that Φ is not the magnitude of the $\nu-\nu$, $\nu-\pi$, or $\pi-\pi$ interactions, although these may be deduced from Φ. The value of R which we have just obtained is somewhat too small. It should be nearer to 9×10^{-13} cm. Utilizing this value and only one of the above equations we find $\Phi\sim110\ mc^2$. From this value of I the heavy particle interaction strength may be deduced in the following manner. In the uranium nucleus 184 particles are in α-groups and 54 neutrons are in ν^2-groups. Each particle in an α-group feels the full force of interaction with 3 others while each particle in a ν^2-group feels only one particle. Therefore the average nuclear particle feels about 2.6 other particles, and the average strength of these interactions is $(110/2.6)\ mc^2$ or $\sim40\ mc^2$.

E. Neutron-Proton Scattering

The very large neutron-proton scattering cross section observed[3] in slow collisions cannot be understood on the basis of the neutron-proton interaction which explains the binding of the deuteron. This probably means that this interaction depends on the relative orientation of the particles' spins. An interaction of strength $\sim40\ mc^2$ and range ϵ^2/mc^2 leads to the observed mass defect of the deuteron, but gives a scattering cross section $\sim10^{-24}$ cm^2, which depends very little on the energy of collision. In the deuteron the neutron and proton have their spins parallel, while in collisions both the parallel and antiparallel situations occur. To explain the cross section we may therefore take a different interaction for the latter case. An interaction of strength $\sim25\ mc^2$ and range ϵ^2/mc^2 will be capable of explaining the collision data.

We are therefore led to the following conclusions concerning the interactions among nuclear particles:

1. They are of an exchange nature with a range $\sim2.8\times10^{-13}$ cm.
2. The $\nu-\nu$ and $\pi-\pi$ interactions are approximately equal.
3. The $\nu-\pi$ interaction probably depends on spin orientation.
4. The strengths of the interactions are of the order of magnitude given below.

$\nu-\pi$	spins	||	$40\ mc^2$	
$\nu-\pi$	spins	a− ||	$25\ mc^2$	(22–28)
$\nu-\nu$ or $\pi-\pi$	spins	a− ||	$33\ mc^2$	(30–36)
$\nu-\nu$ or $\pi-\pi$	spins	||	?	

5. It is possible for a di-neutron or di-proton to be dynamically stable, but unstable with respect to β-decay.

It should be emphasized that the above results are provisional and will certainly have to be modified somewhat. In the first place, the interactions are expressed in terms of an effective "potential hole." This will have to be replaced by some continuous interaction function or functions. Also, the strengths given above depend on the range, which may need to be modified slightly.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month, for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

On the Predissociation in the Sulphur Bands

The phenomenon of predissociation was observed for the first time by V. Henri[1] in the sulphur bands and studied later by several authors. The principal feature consists in the fact that the emission band system abruptly stops at a definite value v', namely, $v'=8$, and also that the last observed band (8,0) is much shorter than the others. The upper limit for the dissociation energy which may be derived is $D=4.41$ ev; G. Herzberg[2] has shown, by considering the character of predissociation, that the right value of the heat of dissociation, is in this case, probably not much lower than this limit.

It is, however, impossible to determine the right value of D from spectroscopic data if the abrupt break of rotational structure has not been observed at least in two successive vibrational levels; the overlapping in the ultraviolet bands makes such a study difficult. We have tried to solve the problem by analyzing the bands (6,28), (6,29), (6,30), (7,29), (7,30), (7,31), (8,30), (8,31) and (8,32). The value of B_{30}'' being lower than that of B_0'' and much nearer to that of B_8' the overlapping in the red region of the band system will not be so important. The dispersion used by us up to the present was not sufficient for a rotational analysis; however, it gave good evidence for the abrupt termination of the rotational structure at 35 cm^{-1} from the head in the $v'=8$ progression and at 92 cm^{-1} in the $v'=7$ progression. The bands of the $v'=6$ progression were almost too broad and the high rotational lines were blended by other bands.

In the (8,0) band at 2829A we have observed the termination of rotational structure at 150 cm^{-1} from the head; according to Naudé and Christy[3] this corresponds to the rotational line $K=37$. Considering the widths of the bands (8; 30,31,32) and (7; 29,30,31), and still using the data of Naudé and Christy we may conclude that there is a predissociation in the $v'=7$ level at about $K=60$.

If we apply the reasoning established by G. Herzberg[2] in the case of P_2 it is easy to show that we have to deal with the I_b case of predissociation, i.e., the perturbing curve producing predissociation has a minimum; the heat of dissociation which may be derived in this case with great precision is equal to 4.41 ± 0.02 ev.

Recent investigations by Badger,[4] Van Dijk and Lameris[5] seem to show that Naudé and Christy's values of B' and B'' are too large. If this is correct, the values derived by us for K should be modified, but the results concerning the shape of the perturbing curve and the energy of dissociation should be the same. Our observations give an approximative determination of $\alpha=(B_v''-B_0'')/v$; we find $\alpha=0.002$. This value may be noticeably in error but the value $\alpha=0.0007$ given by Naudé and Christy is certainly much too low.

A high dispersion analysis is in progress.

BORIS ROSEN
MAURICE DÉSIRANT
JULES DUCHESNE

Department of Astrophysics,
University of Liége, Belgium,
September, 1935.

[1] V. Henri, *Structure des Molécules* (Paris, 1925), p. 93.
[2] G. Herzberg, Ann. d. Physik **15**, 677 (1932); note on p. 701.
[3] S. M. Naudé and A. Christy, Phys. Rev. **37**, 490 (1931).
[4] R. M. Badger, Phys. Rev. **46**, 1025 (1934); see also A. Christy, ibid. **47**, 251 (1935).
[5] E. W. Van Dijk and A. J. Lameris, Physica **2**, 785 (1935).

After Effect of Aluminum Bombarded by Electrons

Using a high voltage Lenard tube, J. J. Livingood and A. H. Snell[1] have searched for the radioactivity induced by electron bombardment, and having been unable to observe it they have attributed the fact to the following four cases: (a) The range of the radiation is less than 4 cm of air, or the periods are either (b) a small fraction of a second or else (c) many hours, or (d) the effect does not exist at the potential used. (In their experiment the voltage applied was 845 kilovolts.) The present investigation has been done with 250–300 kilovolts tube voltage and 1 milliampere tube current. The high speed electrons produced were bombarded upon an aluminum foil placed in high vacuum. After the bombardment, the tube potential was removed and the after effect of aluminum was examined with a Geiger counter. A certain kind of radiation was then observed which decayed with half-value periods of about 7 seconds, 40 seconds and 10 minutes. This radiation was determined later to be an electron radiation, and in the case of 40-second period, the maximum energy was 2.5 kilo-electron volts. These results are not inconsistent with those of Livingood and Snell whose investigation has not been extended to the range of present investigation as mentioned above. The similar effect has also been observed in the case of many elements including Ni, Cu and Ag. It is under investigation whether these are nuclear phenomena or extra-nuclear ones. This investigation has been started by the suggestions of Dr. Y. Nishina, and the author's thanks are due to him and to Professor S. Nishikawa for their kind advice.

MASAMICHI TANAKA

Research Laboratory,
Tokyo Electric Co.,
Kawasaki, Japan.
October 20, 1935.

[1] Livingood and Snell, Phys. Rev. **48**, 485 (1935).

Inhomogeneous Fields for Mass Spectrography

The use of a nonuniform electric field perpendicular to a homogeneous magnetic field provides the possibility of tremendously increasing the dispersion in the mass spectral analysis of ions. A detailed discussion of the case where the fields are uniform has already been given[1] wherein it is demonstrated that the trajectories followed will be cycloids. When, in particular, an electric field E_x^0 superposed on a magnetic field H_z are chosen, the parametric equations for the ion paths are

$$\begin{aligned} x&=\alpha_0+(eE_x^0/m\omega^2)+(A/m\omega)\sin\omega t,\\ y&=\beta_0-(eE_x^0/m\omega)t+(A/m\omega)\cos\omega t, \end{aligned} \tag{1}$$

where $\omega=eH_z/mc$ and α_0, β_0, A are constants of integration. Depending on the initial conditions, the cycloids will be curate, prolate or common; and will be the latter when $\dot{x}_0=cE_x^0/H_z$, $\dot{y}_0=\dot{z}_0=0$. Then, the cusps will lie among a line parallel to the y axis; $\Delta y_c/y_c=\Delta m/m$; further, the addition of the electric field does not disturb the directional refocusing characteristic of ion paths in a uniform magnetic field.

Let E_x now be a function of y. In a qualitative way one can readily see what the resulting effects would be. Suppose that E_x increases with increasing negative values of y. Since the paths followed by the heavier ions will be in a region of greater E_x than those of the lighter ones, the former will spread out more along the y axis, and the dispersion will increase progressively with m in a manner depending on the form of $E_x(y)$. Rigorous solutions of the equations of motion are difficult to obtain in this case; a method of successive approximations is applicable.

Let the zeroth approximation be expressed by Eqs. (1), and choose the linearly varying field

$$E_x=E_x^0+\epsilon y, \quad E_y=E_y^0+\epsilon x. \tag{2}$$

Substitute in (2) the results of (1) obtaining E_x and E_y as functions of the time only, as a first approximation. The equations can then be rigorously solved. One finds

$$\begin{aligned} x&=\alpha_1+e(E_x^0+\epsilon\beta_0)/m\omega^2+(1/m\omega)(K_1\sin\omega t-K_2\cos\omega t)\\ &\qquad+(e/m\omega)(E_y^0+\epsilon\alpha_0)t,\\ y&=\beta_1+e(E_y^0+\epsilon\alpha_0)/m\omega^2+(1/m\omega)(K_1\cos\omega t-K_2\sin\omega t)\\ &\quad-(1/m\omega)\{e(E_x^0+\epsilon\beta_0)t-(e^2\epsilon E_x^0/2m\omega)t^2\\ &\qquad+(e\epsilon A/m\omega^2)\sin\omega t\}, \end{aligned} \tag{3}$$

where α_1, β_1, K_1 and K_2 are, once more, constants of integration. It is a simple matter to solve for the extremal values of x and y as given in (3). One finds that the greater the number of periods taken for these modified cycloids, the more nearly correct becomes the relation $y_m\sim m^2$; a large increase in the dispersion has, therefore, been made possible.

It does not appear desirable at this point to go into details as far as the trajectories given by (3) are concerned until higher approximations have been investigated and other functions giving rise to greater dispersion considered. It is to be pointed out, however, that in order to obtain the full benefit of the large dispersion brought about by the nonuniform field, sharpness in the definition of the traces will probably be sacrificed. Hence it would be of great interest to study the refocusing characteristics of such a field combination. From an experimental point of view, the necessity of increasing the pole-gap separation as well as the precise determination of the nonhomogeneous electric field may offer some difficulties.[2]

S. H. Bauer

Gates Chemical Laboratory,
California Institute of Technology,
October 31, 1935.

[1] L. Page, Phys. Rev. **33**, 553 (1929); **42**, 101 (1932).
[2] F. W. Aston, *Mass Spectra and Isotopes* (Longmans, Green and Co., 1933), p. 77; A. E. Shaw, Phys. Rev. **44**, 1006 (1933).

A New Experimental Method for Study of the Upper Atmosphere

Calculations and laboratory tests indicate that by projecting a *modulated* searchlight beam and measuring the light scattered from sections of its high altitude path at an observing station some kilometers distant, by using a large mirror with a photo-cell and synchronized amplifier, information can be obtained regarding the molecular density and certain other characteristics of the atmosphere in the almost unexplored region from 30 to 70 km, and possibly for even greater heights. A brief description of the method and its possibilities is given in the December, 1935 issue of the *Journal of Terrestrial Magnetism*. This notice is published to reach the attention of workers in numerous other fields who may be interested.

M. A. Tuve
E. A. Johnson
O. R. Wulf

Department of Terrestrial Magnetism
Carnegie Institution of Washington (M.A.T., E.A.J.),
Bureau of Chemistry and Soils
U. S. Department of Agriculture (O.R.W.),
Washington, D. C.,
November 6, 1935.

Doubly Excited States of Helium—A Correction

In a recent article, Wilson[1] noticed a discrepancy between his value for $(2p)^2\,{}^3P$ obtained by Hartree's method, and that obtained by one of us by the variational method.[2] This discrepancy is unfortunately due to an algebraic error in the latter calculation. The correct value obtained by minimizing the integral for $(2p)^2\,{}^3P$ is $(2p)^2\,{}^3P=-1.3976$, and the normalized wave function for ${}^3P$ is

$$\begin{aligned} &(8/9)^{1/2}[Y_{10}(1)\alpha^{5/2}r_1\exp(-\alpha r_1)Y_{11}(2)\beta^{5/2}r_2\exp(-\beta r_2)\\ &\qquad-Y_{10}(2)\alpha^{5/2}r_2\exp(-\alpha r_2)Y_{11}(1)\beta^{5/2}r_1\exp(-\alpha r_1)|, \end{aligned}$$

where $\alpha=0.84$, and $\beta=0.83$. The values for $(2p)^2\,{}^1D$ and $(2p)^2\,{}^1S$ obtained with the variational parameters so determined are $(2p)^2\,{}^1D=-1.326$, $(2p)^2\,{}^1S=-1.217$. Thus the value $(2p)^2\,{}^3P=-1.3976$ from the variational method is quite close to Wilson's value -1.4018.

Ta-You Wu
S. T. Ma

National University of Peking,
October 24, 1935.

[1] Wm. Wilson, Phys. Rev. **48**, 536 (1935).
[2] Ta-You Wu, Phys. Rev. **46**, 239 (1934).

The Value of the Electronic Charge

Kellström's[1] recent determination of the viscosity of air seems to furnish the final piece of evidence required to establish the essential correctness of the so-called grating value of the electronic charge e. As is well known, there has been for a number of years a sharp discrepancy between the value of e given by oil-drop work and that deduced from the absolute wave-lengths of x-rays, as determined by means of a grating. In recalculating the oil-drop data, in 1929,[2] I adopted Millikan's assumed value of the viscosity of air ($\eta_{23}=1822.7\times10^{-7}$), and also his assumed probable error (0.05 percent), since I did not feel competent to express an expert opinion in that field. This value had been obtained by the method of rotating cylinders, a method that has generally been considered more reliable than the method of capillary tubes. I thus obtained $e=(4.768\pm0.005)\times10^{-10}$ e.s.u., as the final result of Millikan's oil-drop work.

Shiba[3] was perhaps the first to challenge the correctness of Millikan's assumption regarding the viscosity of air. He presented a table of values of η which indicated clearly that the capillary tube method gives in general a definitely higher result than the rotating cylinder method. Shiba himself adopted 1831.2×10^{-7} as the best average value. Now, however, Kellström, using the method of rotating cylinders, obtains $(1834.8\pm3.0)\times10^{-7}$, an even higher value. The use of this last value with Millikan's data leads to $e=(4.816\pm0.013)\times10^{-10}$ e.s.u.

Meanwhile, as Bearden[4] has recently shown, all measurements on the absolute wave-lengths of x-rays are remarkably consistent. These results can be used to determine a value of e only if one assumes a geometrically perfect crystal (in practice, calcite), and certain observed constants (density, etc.) for this crystal. With such an assumption, and with the latest values of the constants, one obtains, in agreement with Bearden,[4] $e=(4.8036\pm0.0005)\times10^{-10}$ e.s.u. Hence there is no longer any outstanding discrepancy between the values of e determined by these two distinctly different methods.

This fact, however, does not settle the problem of the values of the three interrelated constants e, e/m, and h. As a result of a number of recent investigations on e/m, it seems more than probable that its true value lies between 1.757 and 1.758 ($\times10^7$ abs. e.m.u.). Let us adopt 1.7575×10^7 as the best average. To get a value of the Planck constant h, one may now use Bohr's formula for the Rydberg constant, a formula that is still believed by theoretical physicists to be correct to a high degree of accuracy. With $e=4.8036$ and $e/m=1.7575$, one obtains $h=6.6286\times10^{-27}$ erg·sec.

About a year ago[5] I presented a diagram showing all important experimental results involving e, e/m, and h. This diagram indicated only too clearly the impossibility of assigning *any* set of values to these three constants that would even reasonably satisfy all of the experimental results. This situation still remains essentially unchanged. The set of values that I gave then was $e=4.768$, $e/m=1.7574$, $h=6.547$. A few of the experimental results are equally well satisfied by either set of values, but in general the two sets predict very different experimental results. Thus if the new set ($e=4.8036$, etc.) is correct, the experimental results for the limit of the continuous x-ray spectrum, as a function of voltage, are all in error by amounts up to 20 times the assigned probable error. These various results, however, are quite consistent, and the method is usually considered especially reliable. Similarly the average value of h/e, from determinations of ionization and resonance potentials, is in error by some five times its apparent probable error. The determinations of h/e from the photoelectric effect and from the value of the radiation constant c_2, are equally in error.

It appears to me that the most desired experiment in this field, at the present time, is a really reliable determination of h/e. Since the two sets of values of e and h that have been discussed give values of h/e differing by 0.58 percent, it should be possible to distinguish between them.

It may be noted, in closing, that the new set of values of e, h, and e/m, leads to $1/\alpha=137.06$. If one retains the same value of e/m (1.7575), but shifts e from 4.8036 to 4.810, $1/\alpha$ becomes exactly 137, and h becomes 6.6433.

RAYMOND T. BIRGE

University of California,
November 15, 1935.

[1] G. Kellström, Nature **136**, 682 (1935).
[2] R. T. Birge, Rev. Mod. Phys. **1**, 1 (1929).
[3] K. Shiba, Inst. Phys. and Chem. Research, Tokyo, Sci. Papers **19**, 97 (1932).
[4] J. A. Bearden, Phys. Rev. **47**, 883 (1935).
[5] R. T. Birge, Science **79**, 438(A) (1934).

Note on Majorana's Exchange Energy

The exchange energy introduced by Majorana is $\Sigma_{i>j}J(r_{ij})P_{ij}=V$, where i, j refer to protons and neutrons, respectively, and P_{ij} is the exchange operator which interchanges the space coordinates x_1^i, x_2^i, x_3^i of the proton i with the space coordinates ξ_1^j, ξ_2^j, ξ_3^j of the neutron j, and r_{ij} is the distance between i and j. The interaction energy operator V is Hermitian and it commutes with the three components of the total momentum operator

$$(\hbar/i)(\Sigma_i\partial/\partial x_s^i+\Sigma_j\partial/\partial\xi_s^j)=G_s.$$

It is satisfactory in these respects. There is, however, an undesirable feature of this interaction energy which is due to the difference of the mass μ of the neutron and the mass m of the proton. It shows itself in an improper behavior of the center of mass and a lack of invariance to Galilean transformations. The coordinates of the center of mass $X_s=(\Sigma m x_s^i+\Sigma\mu\xi_s^j)/(\Sigma_i m+\Sigma_j\mu)$ have the following equations of motion

$$\frac{dX_s}{dt}=\frac{G_s}{M}+\frac{i(m-\mu)}{\hbar M}\sum_{(i>j)}J(r_{ij})(\xi_s^j-x_s^i)P_{ij}.$$

Here M is the total mass. If $m=\mu$ this is the usual relation between the velocity of the center of mass and the momentum. Because of the extra term in $m-\mu$ there is an additional tremblatory component in the motion of X_s somewhat analogous to Schrödinger's "Zitterbewegung."

The lack of invariance to Galilean transformations can be seen by considering the deuteron. The solutions corresponding to an energy E and a momentum G are obtained by the substitution $\psi=\varphi(y)\exp\{(i/2\hbar)\Sigma(x_s+\xi_s)G_s\}$ with $y=\xi-x$ which gives

$$-\frac{\hbar^2}{2}\left(\frac{1}{\mu}+\frac{1}{m}\right)\Sigma_s\frac{\partial^2\varphi(y)}{\partial y_s^2}+\frac{\hbar}{2i}\frac{\mu-m}{\mu m}\Sigma_s G_s\frac{\partial\varphi(y)}{\partial y_s}+J(y)\varphi(-y)$$
$$=\left[E-\frac{G^2}{8}\left(\frac{1}{m}+\frac{1}{\mu}\right)\right]\varphi(y). \quad (1)$$

The operator on the left side of this equation is Hermitian and $E-(G^2/8)(1/m+1/\mu)$ has real eigenwerte. It should be noted that the substitution $\psi=\chi(y)\exp\{(i/\hbar)\Sigma_s \times(mx_s+\mu\xi_s)G_s/(m+\mu)\}$ leads to a non-Hermitian operator for $E-G^2/2(m+\mu)$. There is thus no freedom in the choice of the substitution and the energy values are determined by Eq. (1). If instead of using the Majorana operator one used ordinary potential forces, the term in $\mu-m$ would be absent and $(G^2/8)(1/m+1/\mu)$ would be changed into $G^2/2(m+\mu)$. These two effects do not compensate in general because the change in E due to the term in $\mu-m$ depends on φ and hence on J. It is thus impossible to interpret the eigenwerte of E as the sum of $G^2/2(m+\mu)$ and an internal energy independent of G.

These anomalies are clearly due to the fact that every exchange of the positions of a neutron and a proton changes the position of the center of mass. The anomalies can be avoided by modifying the operator. A simple change leading to the desired result is to use instead of P_{ij} an operator P_{ij}' defined by

$$P_{ij}'\psi(\cdots,x^i,\cdots;\cdots,\xi^j,\cdots)$$
$$=\psi\left(\cdots,\xi^j+\frac{\mu-m}{\mu+m}(\xi^j-x^i),\cdots;\right.$$
$$\left.\cdots,x^i+\frac{\mu-m}{\mu+m}(\xi^j-x^i),\cdots\right).$$

This operator P' leaves unchanged the center of mass of the neutron-proton pair. It is Hermitian, commutes with the total momentum, and with the center of mass. The wave equation modified by changing P into P' leads to results invariant under Galilean transformation. In ordinary calculations of mass defects and similar problems it is practically indistinguishable from P on account of the smallness of $(\mu-m)/(\mu+m)$.

It is not probable however that such a complicated interaction energy can have the significance of a fundamental law of nature. It would be more satisfactory to have a general theory in which the Majorana force is the first term of an expansion in $(\mu-m)/(\mu+m)$.

G. Breit
E. Wigner

The Institute for Advanced Study,
Princeton University,
November 14, 1935.

Proton-Proton Forces in Anomalous Scattering and in Nuclear Binding

Recent experiments by White[1] on the scattering of 600–750 kv protons in hydrogen show large deviations from the theoretical cross sections calculated by quantum mechanics and indicate a departure from the Coulomb law at a distance of about 5×10^{-13} cm. Using the Feenberg-Knipp nuclear model, discussed elsewhere in this issue, we have calculated the scattering cross sections on the assumption that the interaction between two protons includes, in addition to the usual Coulomb repulsion, an attractive interaction $-A_{\pi\pi}e^{-(r/a)^2}$ with $a=2.2\times10^{-13}$ cm and $A_{\pi\pi}$ adjusted to fit the experimental scattering at 45°. The value of $A_{\pi\pi}$ so determined (45 mc^2), is in very satisfactory agreement with the value obtained by Feenberg and Knipp (41 mc^2), when the binding problems are treated with a mixed Majorana and Heisenberg potential for neutron-proton interaction. These calculations have been repeated with a rectangular potential hole under varied conditions.

When the calculations are extended to other angles of scattering we encounter the gravest difficulties. It is readily seen that when the phase shift K_0, which represents the effect of the modified field on the s scattering, is adjusted to fit the observed scattering at 45°, it is impossible to get agreement with the scattering at other angles. This result is entirely independent of the type of potential assumed for interaction at small distances. Both the theoretical and the observed scattering show a minimum in the neighborhood of 30° in contrast to the Mott-Coulomb scattering which decreases monotonically with increasing angle up to 45°. However, the theoretical scattering at 30°, when a fit is made at 45°, is over six times as large as the experimental. White's results are undoubtedly subject to large statistical fluctuations, as may be seen from irregularities in the data and from the fact that at 30° the observations correspond actually to about four proton collisions. Nevertheless the disagreement seems too considerable to dismiss cavalierly in this way. One alternative that remained open was to investigate the possible influence of p scattering on the angular distribution. If this were to be of importance an immediate consequence would be the breakdown of the Coulomb law at the unbelievably large distance of 2×10^{-12} cm. Examination reveals that the modification in the scattering produced by a distortion of the p wave is zero at 45° and much too small at 30° to reduce the scattering to White's value. Here one adjusts the phase shift K_0 for s scattering to give a fit at 45°, and then the phase shift K_1 for p scattering is varied to minimize the scattering at 30°. If a smaller value of K_0 is used so as to obtain a theoretical scattering at 45° about 0.8 of the experimental, it is still impossible to fit the scattering at 30° by a suitable choice of K_1. It is to be emphasized that these conclusions are completely independent of the nuclear model. They are true even if the potential is not centrally symmetric or depends in some way on the relative momentum or spin orientation. Moreover, they must remain true even if the wave mechanics breaks down for small distances, since only the asymptotic form of the wave function is involved (in a region where wave mechanics is known to be accurate) and any future theory must reproduce the same expression. Distortion of the higher order harmonics would be entirely negligible, for the de Broglie wave-length of the fastest protons (7×10^{-12} cm) is so large compared with the range below 5×10^{-13} cm where departures from the Coulomb law occur that the wave function must have there an appreciably

constant amplitude. Thus it appears impossible in any way to account for the experimental results. Further experimental work is urgently needed to confirm or preclude the possibility that these discrepancies may be due to statistical fluctuations or systematic error.

A discussion of the calculations with the nuclear model will shortly appear in a more extended form in this journal. This work was originally suggested to me by Dr. Eugene Feenberg, to whom I am grateful for much friendly and valuable discussion. I also wish to thank Dr. M. G. White for communicating to me unpublished data.

R. D. PRESENT

Purdue University,
Lafayette, Indiana,
November 13, 1935.

[1] M. G. White, Phys. Rev. **47**, 573 (1935).

THE AMERICAN INSTITUTE OF PHYSICS

INCORPORATED

GOVERNING BOARD

For The American Physical Society:

KARL T. COMPTON, *Chairman*
Massachusetts Institute of Technology

GEORGE B. PEGRAM, *Secretary*
Columbia University

JOHN T. TATE
University of Minnesota

For The Optical Society of America:

E. C. CRITTENDEN
Bureau of Standards

PAUL D. FOOTE
The Gulf Companies

F. K. RICHTMYER
Cornell University

For The Acoustical Society of America:

HARVEY FLETCHER
Bell Telephone Laboratories

VERN O. KNUDSEN
University of California at Los Angeles

WALLACE WATERFALL
The Celotex Corporation

For The Society of Rheology:

E. C. BINGHAM
Lafayette College

A. STUART HUNTER
du Pont Rayon Company

S. E. SHEPPARD
Eastman Kodak Company

For The American Association of Physics Teachers:

HOMER L. DODGE
University of Oklahoma

PAUL E. KLOPSTEG
Central Scientific Company

FREDERIC PALMER
Haverford College

ADMINISTRATIVE STAFF

HENRY A. BARTON, *Director* JOHN T. TATE, *Adviser on Publications*

MADELINE M. MITCHELL, *Editorial Secretary*

Office: 11 East 38th Street, New York, New York

JOURNALS

THE PHYSICAL REVIEW

REVIEWS OF MODERN PHYSICS

PHYSICS
JOHN T. TATE, *Editor*
J. W. BUCHTA, *Assistant Editor*
E. C. BINGHAM, *Rheology Editor*

THE JOURNAL OF THE OPTICAL SOCIETY OF AMERICA

THE REVIEW OF SCIENTIFIC INSTRUMENTS
WITH PHYSICS NEWS AND VIEWS
F. K. RICHTMYER, *Editor*

JOURNAL OF THE ACOUSTICAL SOCIETY OF AMERICA
F. R. WATSON, *Editor*

THE JOURNAL OF CHEMICAL PHYSICS
HAROLD C. UREY, *Editor*

THE AMERICAN PHYSICS TEACHER
DUANE ROLLER, *Editor*

The American Institute of Physics is a membership corporation of which five societies are the founding members. These five societies are the principal national societies devoted to pure and applied physics in America. Their names, and those of their representatives who form the Governing Board of the Institute, are given above. The principal work of the Institute is the publication of journals sponsored by the societies or by itself. The names and the editors of the journals are also listed above.

The broad purpose of the Institute is to represent, in all matters of wide or common interest, the five thousand or more members and subscribers associated with the Founder Societies and the journals. It aims to advance the science and profession of physics, and to promote cooperation between pure research, the applied sciences and the industries. To achieve these aims, it is greatly in need of an endowment and is empowered by law to administer grants and funds of any kind.

CONTENTS

PHYS. REV. 48 (1935) DECEMBER 1

Search for Radioactivity Induced by 800-Kilovolt Electrons . . . . . J. J. LIVINGOOD AND ARTHUR H. SNELL 851

Two Radioactive Substances from Magnesium after Deuteron Bombardment . . . . . M. C. HENDERSON 855

Infrared Absorption Spectrum of Germane . . . . . WENDELL B. STEWARD AND HARALD H. NIELSEN 861

Infrared Absorption Bands of Methane . . . . . ALVIN H. NIELSEN AND HARALD H. NIELSEN 864

Interaction Between Vibration and Rotation for Symmetrical Molecules . . . . . MANFRED JOHNSTON AND DAVID M. DENNISON 868

Geiger-Counter Characteristics with Applied Potentials Reversed . . . . . D. B. COWIE 883

High Current Ion Sources for Nuclear Investigations . . . . . E. S. LAMAR, E. W. SAMSON AND K. T. COMPTON 886

Polymorphism, Principally of the Elements, up to 50,000 kg/cm² . . . . . P. W. BRIDGMAN 893

Intranuclear Forces . . . . EUGENE FEENBERG AND JULIAN K. KNIPP 906

Note on the Interaction of Nuclear Particles . . . . LLOYD A. YOUNG 913

Letters to the Editor:

On the Predissociation in the Sulphur Bands . . . . . BORIS ROSEN, MAURICE DÉSIRANT AND JULES DUCHESNE 916

After Effect of Aluminum Bombarded by Electrons . . MASAMICHI TANAKA 916

Inhomogeneous Fields for Mass Spectrography . . . . . S. H. BAUER 917

New Experimental Method for Study of the Upper Atmosphere . . . . . M. A. TUVE, E. A. JOHNSON AND O. R. WULF 917

Doubly Excited States of Helium—A Correction . TA-YOU WU AND S. T. MA 917

Value of the Electronic Charge . . . . . RAYMOND T. BIRGE 918

Note on Majorana's Exchange Energy . . . . . G. BREIT AND E. WIGNER 918

Proton-Proton Forces in Anomalous Scattering and in Nuclear Binding . . . . . R. D. PRESENT 919

LANCASTER PRESS INC., LANCASTER, PA.